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Synthesis and self-assembly of 5,5'-bis(phenylethynyl)-2,2'-bithiophene-based bolapolyphiles in triangular and square LC honeycombs

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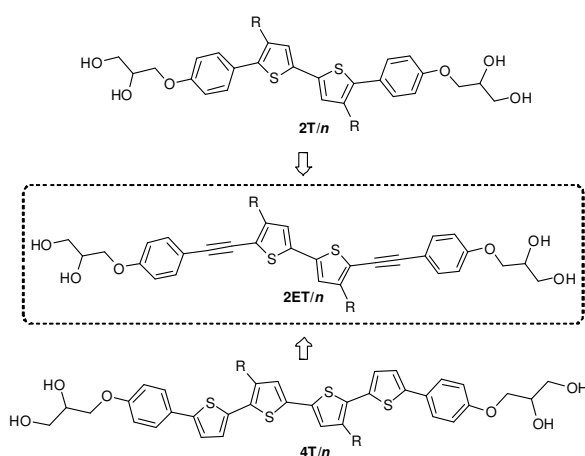
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1. Introduction

Creation of well-defined nanostructures through ingenious molecular self-assembly is of current interest for numerous advanced technological applications.¹ Examples are metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) forming solid state structures with square or hexagonal channels providing permanent porosity for storage and catalysis applications.² Moreover, MOFs and COFs involving π -conjugated aromatic building blocks created significant interest as candidates for semiconducting organic materials.³ Remarkably, very similar polygonal honeycomb structures, having an even wider range of different cylinder shapes, ranging from triangular via square, pentagonal to hexagonal and beyond, were recently obtained in the fluid, liquid crystalline (LC) state,^{4,5,6,7,8} being a unique state of soft matter combining order and mobility on a molecular to macroscopic level.^{6,9} The majority of these fluid honeycombs are formed by polyphilic rod-like molecules with flexible lateral chains, the chains filling the hollow space inside the honeycomb cells and contributing to the fluidity of the self-assembled overall superstructures.¹⁰ Another source of mobility arises from the dynamic character of the hydrogen bonding networks between the polar glycerol groups located at both ends of the rod-like and lipophilic cores, interconnecting the aromatic rods to network structures. Thus, the rigid and geometrically fixed metal coordination sites and covalent linkages used in solid state MOFs and COFs, respectively, are replaced by dynamic hydrogen bonding networks located at the ends of these T-shaped^{4,5} or X-shaped¹¹ bolapolyphilic LC molecules.¹² This leads to unique fluids with compartmented honeycomb structures, representing columnar LC phases with π -conjugated rod-like cores laying perpendicular to the column long axis and forming cell walls enclosing channels filled by the lateral chains. This unique mode of soft self assembly was confirmed experimentally⁵ and supported by simulation work.¹³ Due to the dynamic character of these structures and the combination of order and mobility, they can be affected by external stimuli, providing supramolecular self-assembled systems for diverse applications. Moreover, as a result of the inherent mobility, transitions between honeycombs with distinct geometries can easily be achieved^{5,6}. Among them, the transition between triangular and square honeycombs is of special interest, because the combination of both types of cells in a uniform structure could lead to periodic and quasiperiodic arrays combining triangular and square cylinders in distinct ratios.^{5,6, 14, 15, 16 a,b} Oligo(phenylene)s and oligo(phenylene ethynylene)s have predominately been used as rigid rod-like cores for the design of T-shaped and X-shaped bolapolyphiles.^{4,5,6,11} In order to introduce functionality into these soft nanostructures for use in potential application, also oligothiophene segments were employed as rod-like building blocks.^{17,18,19,20,21} Honeycomb-type columnar phases with triangular ($Col_{hex}\Delta/p6mm$), square ($Col_{squ}/p4mm$) and hexagonal cells ($Col_{hex-6}/p6mm$) have been found for these compounds based on

bithiophene (**2T/n**, Scheme 1),^{18,19} tetrathiophene (**4T/n**)²⁰ and hexathiophene cores²¹ by variation of the length and the number of lateral alkyl chains.

Besides these oligothiophenes, compounds involving additional ethynylene units are also attractive for providing electron conducting²² and fluorescent properties.²³ Herein we report a new series of dithiophene based X-shaped bolapolyphiles **2ET/n**, incorporating additional ethynylene units (**E**) in the rigid core and compare them with the related compounds **2T/n** and **4T/n** without these ethynylene units (see Scheme 1). Such compounds can be considered as being intermediate between compounds **2T/n** and **4T/n** because they contain dithiophene units just like the **2T/n** series and have almost the same core length just like the tetrathiophene-based bolapolyphiles **4T/n**.



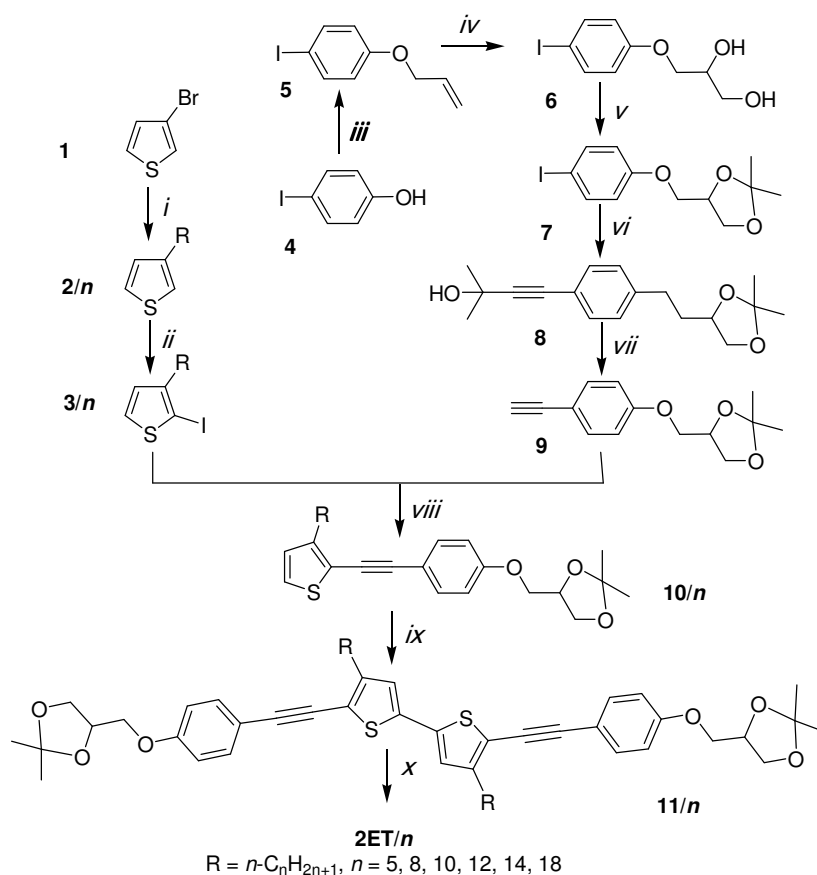
Scheme 1 Compounds **2ET/n** under investigation and the related previously reported dithiophene-based bolapolyphiles **2T/n**¹⁹ and tetrathiophene-based bolapolyphiles **4T/n**.²⁰

2. Results and discussion

2.1 Synthesis

The 5,5'-bis(phenylethynyl)-2,2'-bithiophene based bolapolyphiles **2ET/n** have been synthesized via Kumada and Sonogashira coupling reactions as key steps, as shown in Scheme 2. Accordingly, 3-alkylthiophenes **2/n**, obtained by Kumada coupling of 3-bromothiophene (**1**) with appropriate *n*-alkyl magnesium bromides,²⁴ were iodinated in 2-position with *N*-iodosuccinimide (NIS)²⁵ and then coupled with the 1,2-O-isopropylidene glycerol substituted phenylacetylene **9** in a Sonogashira coupling reaction,²⁶ leading to the 2,3-disubstituted thiophenes **10/n**. Lithiation in 5-position and Cu²⁺ promoted oxidative coupling²⁷ provided the 2,2'-dithiophenes **11/n**. The 1,2-O-isopropylidene glycerol units of these compounds **11/n** were then deprotected to give the final compounds **2ET/n**. The phenylacetylene building

block **9** was prepared from 4-iodophenol (**4**) by allylation, OsO₄-catalyzed 1,2-dihydroxylation, followed by protection of the 1,2-diol group as 1,2-O-isopropylidene ketal,²⁸ and subsequent Sonogashira coupling with 2-methyl-3-butyn-2-ol and alkaline deprotection of the ethynyl group.²⁶ The final compounds were purified by repeated crystallization from petroleum ether: ethyl acetate = 1 : 1. The detailed procedures and corresponding analysis data are collected in the Supporting Information. Compounds **2ET/n** were studied by POM, DSC and XRD, as described in the following sections.



Scheme 2 Synthesis of compounds **2ET/n**. *Reagents and conditions:* (i) C_nH_{2n+1}MgBr, Ni(dppp)Cl₂, THF, reflux, 15 h, 75-86%; (ii) NIS, CH₂Cl₂, CH₃COOH, RT, 2 h, 90-95%; (iii) 3-bromoprop-1-ene, K₂CO₃, CH₃CN, reflux, 15 h, 92%; (iv) OsO₄, NMMNO, H₂O, acetone, RT, 80%; (v) 2,2-dimethoxypropane, PPTS, 96%; (vi) 2-methylbut-3-yn-2-ol, THF, Et₃N, Pd(PPh₃)₄, CuI, 89%; (vii) KOH, toluene, reflux, 15 h, 88%; (viii) THF, Et₃N, Pd(PPh₃)₄, CuI, 77-85%; (ix) *n*-BuLi, THF, CuCl₂, -60 °C, 15h, 65-80%; (x) 10% HCl, CH₃OH, 25 °C, 15 h, 60-67%.

2.2 LC self-assembly of compounds **2ET/n**

The phase transition temperatures and associated enthalpy values of the synthesized compounds are summarized in Table 1. Compounds **2ET/n** with *n* = 8, 10 and 18 exhibit enantiotropic

(thermodynamically stable) LC phases, whereas compound **2ET/5** with the shortest chains is non-mesomorphic and compounds **2ET/12** and **2ET/14** with medium chain length display only monotropic (metastable) LC phases which rapidly crystallize on cooling. In this homologous series the mesophase stability, i.e. the LC-Iso transition temperature, decreases with growing chain length and after a local minimum between $n = 12$ and 14 it slightly rises again ($n = 18$).

Table 1 Phase types, phase transition temperatures with corresponding enthalpy values, lattice parameters and other parameters of the bolapolyphiles **2ET/n**^a together with the related oligothiophenes **2T/n**¹⁹ and **4T/n**²⁰ reported previously.^b

Compd.	$T^{\circ}\text{C}$ [$\Delta H/\text{kJ mol}^{-1}$]	a/nm	n_{cell}	n_{wall}	f_{R}
2ET/5	Cr 170 ^f Iso				0.29
2ET/8	Cr < 20 ^d Col _{hex} $\Delta/p6mm$ 114/111 ^e [1.1] Iso	3.20	3.38	1.13	0.39
2ET/10	Cr 90 [43.5] Col _{hex} $\Delta/p6mm$ 114/112 ^e [1.5] Iso	3.20	3.08	1.03	0.44
2ET/12	Cr 115 [74.9] (Col _{hex} $\Delta/p6mm$ 91 ^e [1.0]) Iso	-	-	-	0.49
2ET/14	Cr 113 [59.9] (Col _{sq} $/p4mm$ 67 ^e [0.8]) Iso	3.15	2.95	1.48	0.52
2ET/18	Cr 26 [20.6] Col _{sq} $/p4mm$ 73/67 ^e [2.5] Iso	3.25	2.73	1.37	0.58
2T/8	Cr 56 Iso	-	-	-	0.41
2T/10	Cr 76 (Col _{sq} $/p4mm$ 71/65 ^d) Iso	2.73	2.73	1.4	0.46
2T/12	Cr < 20 ^c Col _{sq} $/p4mm$ 71/66 ^e Iso	2.78	2.60	1.3	0.51
2T/14	Cr 50 Col _{sq} $/p4mm$ 57/46 ^e Iso	2.87	2.57	1.3	0.55
2T/18	Cr 55 (Col _{hex} $\Delta/p6mm$ 45/34 ^e) Iso	4.60	4.94	1.7	0.61
4T/5	Cr 186 (SmA ⁺ 152 Iso)	-	-	-	0.25
4T/8	Cr 139 Col _{hex} $\Delta/p6mm$ 171 Iso	3.74	4.13	1.4	0.35
4T/10	Cr 123 (Col _{sq} $/p4mg$ 75/68 ^e) Col _{hex} $\Delta/p6mm$ 162 Iso	3.64	3.68	1.2	0.40
4T/12	Cr 138 (Col _{sq} $/p4mm$ 125 N _{cyb} 135) Iso	3.52	3.69	1.8	0.44
4T/14	Cr 140 Col _{sq} $/p4mm$ 147 Iso	3.48	3.37	1.7	0.48
4T/18	Cr 100 Col _{sq} $/p4mm$ 141 Iso	3.63	3.16	1.6	0.54

^a Determined by DSC (5 K min⁻¹, peak temperature, second scans) and confirmed by POM, for the LC-Iso phase transition peak temperatures from the first heating/first cooling scan are given; values in (round) parentheses refer to monotropic phases; a = lattice parameters as determined by XRD; n_{cell} = number of molecules per unit cell, as determined from a and assuming a height of $h = 0.45$ nm (for details of the estimations, see Table S2 in Supporting Information); n_{wall} = number of molecules arranged in the cross section of the honeycomb walls; f_{R} = volume fraction of the lateral alkyl chains; abbreviations of the phases: Cr = crystalline solid, Iso = isotropic liquid, Col_{hex} $\Delta/p6mm$ hexagonal columnar phase with plane group $p6mm$ (triangular cylinders), Col_{sq} $/p4mm$ = square columnar phase with plane group $p4mm$ (square cylinders), Col_{hex} $\Delta/p6mm$ hexagonal columnar phase representing a hexagonal honeycomb; ^b for the reference compounds only data of $p6mm$ and $p4mm$ phases for one selected temperature are given, for more details, see refs. [19, 20] ^c Temperature determined by POM. ^d No crystallization was observed even after storage for several weeks. ^e Phase transition temperature on cooling.

Between crossed polarizers, the textures of all LC phases show birefringent, in most cases spherulitic textures as typical for LC phases with 2D periodicity (columnar phases; see Figs. 1a, e and S1). All these columnar phases are uniaxial as indicated by the presence of optically isotropic homeotropic regions, where the direction of the cylinder long axis is perpendicular to the substrate surfaces (dark areas in Figs. 1a, e and S1). This means that the investigated columnar phases could either have a hexagonal or a square 2D lattice. Investigation with an additional λ retarder plate shows that all columnar phases are optically negative, i.e. they have the high index optical axis, which is known to be parallel to the long axis of the π -conjugated cores, perpendicular to the column long axis (see Figs. 1b, f). This is in line with polygonal honeycomb structures in which the π -conjugated rod-like cores are arranged on average perpendicular to the cylinder long axis.

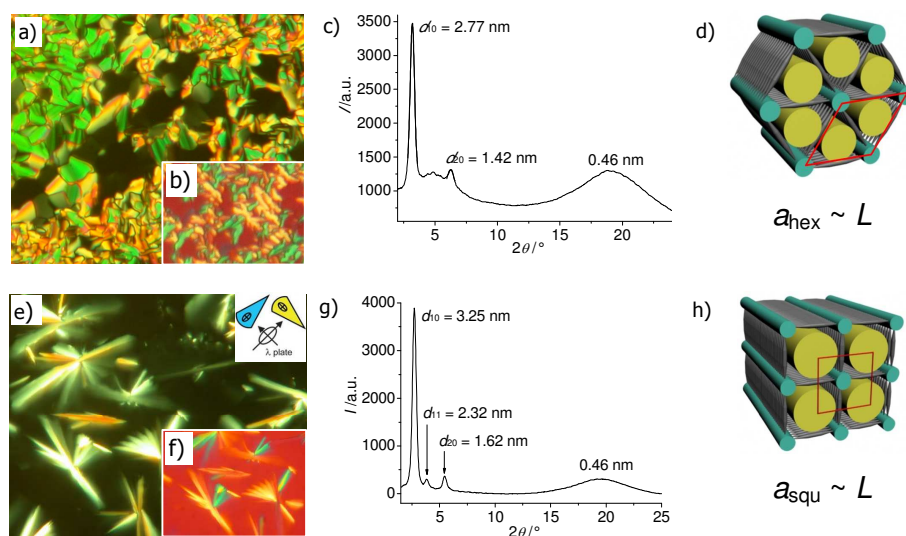


Fig. 1 Mesophases of compounds **2ET/n**: (a) Texture (crossed polarizers, $T = 80\text{ }^{\circ}\text{C}$); (b) texture with λ retarder plate; (c) XRD pattern ($T = 100\text{ }^{\circ}\text{C}$) and (d) model of the $\text{Col}_{\text{hex}}\Delta/p6mm$ phase of compound **2ET/10**; (e) texture ($T = 60\text{ }^{\circ}\text{C}$); (f) texture with λ retarder plate; (g) XRD pattern ($T = 25\text{ }^{\circ}\text{C}$) and (h) model of the $\text{Col}_{\text{squ}}/p4mm$ phase of compound **2ET/18**. The indicatrix-orientation of the λ -plate is shown in an inset in (e). The diffuse scattering in the small angle region of the XRD pattern of compound **2ET/10** is also observed at $T = 25\text{ }^{\circ}\text{C}$ (see Fig. S6) and for the $\text{Col}_{\text{hex}}\Delta/p6mm$ phase of **2ET/8** (Fig. S5) and therefore, it is likely be due to a defective structure of the triangular cylinders, effectively representing rhombic cells which are randomly distributed along the tree main axes of the hexagonal lattice, as previously suggested for the Col_{hex} phases of compounds **4T/n**,²⁰ hence, the model (d) shows a simplified and idealized picture neglecting these defects.

The XRD patterns of compounds **2ET/n** ($n = 8, 10, 14$ and 18) show diffuse wide-angle scatterings with maxima around $0.44\text{--}0.46\text{ nm}$, confirming that they form true LC phases (see Figs. 1c,g, and S5-8). Indexing of the SAXS patterns led to the phase assignments with plane groups as shown in Table 1. For the compounds **2ET/8** and **2ET/10** the ratio of reciprocal small-angle X-ray spacings is 1:2. A simple lamellar organization can be excluded based on the typical textures, indicating optically negative and uniaxial columnar phases (Figs. 1a and S1a). Thus, the small angle reflexes of the diffraction patterns were indexed as 10 and 20 reflections of hexagonal lattices with $a_{\text{hex}} = 3.20\text{ nm}$. These values are in the range of the molecular length ($L_{\text{mol}} = 3.10\text{--}3.35\text{ nm}$), $L_{\text{mol}} = 3.35\text{ nm}$ being the largest possible length in the most stretched conformation and measured between the ends of the primary hydroxyl groups at both ends of the rod-like core (see Fig. 2). The same coincidence of L_{mol} and a_{hex} was previously observed for the $\text{Col}_{\text{hex}}\Delta/p6mm$ phases of the related compounds **4T/n** ($n = 8, 10$, see Table 1).²⁰ Presently there are three known types of LC honeycombs with hexagonal symmetry formed by X-shaped bolpolyphilic (triphilic) molecules, having different relations between the hexagonal lattice parameter a_{hex} and molecular length

between the ends of the terminal polar groups (L_{mol}). These are the triangular honeycomb, where $a_{\text{hex}} = L_{\text{mol}}$,^{7,18,19,20,21} the hexagon tiling⁴ with $a_{\text{hex}} = 3^{1/2} L_{\text{mol}}$ and the Kagome pattern, combining hexagonal and triangular cells and having a ratio $a_{\text{hex}} = 2 L_{\text{mol}}$.^{11b} The latter is only formed by molecules with two different and incompatible lateral chains as well as honeycomb super lattices combining honeycomb cells with different content (see Fig. S3).^{11c,d} The regular rhomb tiling with a relation $a_{\text{hex}} = 3^{1/2} L_{\text{mol}}$, the same as for the hexagon tiling, has not been found so far. The coincidence of L_{mol} and a_{hex} is unique for the tiling by equilateral triangles in the $\text{Col}_{\text{hex}}\Delta/p6mm$ phase, as previously observed for the related compounds **4T/n** ($n = 8, 10$, see Table 1).²⁹ The number of molecules organized around the triangular cells can deviate from being exactly three, because in the LC state the individual molecules do not have fixed positions, thus this number is even not necessarily any integer number, but represents a time and space averaged value. Each of the three walls enclosing a triangular honeycomb cell should be at least one aromatic core in (lateral) diameter, but occasionally also two molecules (or even three) can be organized either side-by-side or in a staggered mode. The resulting average number of molecules organized laterally in each of the honeycomb walls (n_{wall}) is estimated by dividing the unit cell volume (assuming a stratum with a height of 0.45 nm, approximately corresponding to the average diameter of the rotationally disordered aromatic cores and corresponding to the maximum of the wide angle scattering in XRD) by the molecular volume (estimated using tabulated crystal volume increments³⁰ as described in Table S2), and then divided by the number of walls per unit cell, i.e. by 3 for the triangular and the hexagon tiling and by two for the square tiling. The estimated number of molecules arranged laterally side by side in the cross section of the honeycomb walls (n_{wall}) is between 1.0 and 1.1 for the triangular honeycombs of compounds **2ET8-2ET12** (see Tables 1 and S2), in line with honeycomb walls formed by (on average) a single molecule in the cross section.

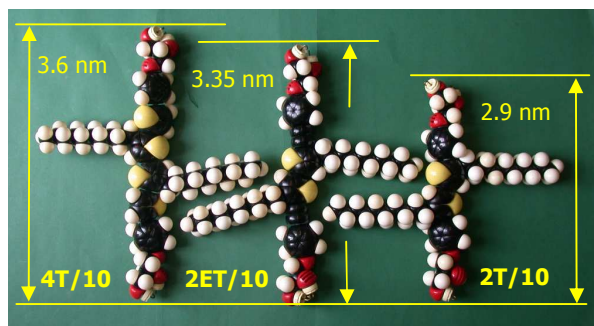


Fig. 2 CPK models and estimated molecular lengths (L_{mol}) of compounds **2ET/n** and the related compounds **2T/n** and **4T/n** ($n = 10$), shown in their most extended conformation.

As the available space within triangular cylinders is restricted, a frustration arises from the overcrowding of the honeycomb cells as the chain length grows further. Therefore, the LC phase stability decreases at the transition from **2ET/10** ($T_{\text{Iso-LC}} = 112$ °C) to **2ET/12** ($T_{\text{Iso-LC}} = 91$ °C, see Table 1). Compounds **2ET/12** and **2ET/14**, with medium lateral chain length, show LC phases only on cooling (monotropic phases, see Figs. S2c,d). Because of rapid crystallization during exposure time of XRD measurement, confirmation of the LC phase structure of compound **2ET/12** was not possible in this way. However, investigations of binary mixtures provide evidence, that the columnar phase of **2ET/12** is a hexagonal columnar phase with triangular honeycomb structure, just like that of **2ET/10**. This is indicated by the continuous growth of the spherulitic texture of the $\text{Col}_{\text{hex}}\Delta/p6mm$ phase of compound **2ET/10** into the region of **2ET/12** without any intermediate minimum, maximum or visible miscibility gap (see Figs. 3a and S4). In contrast, in the contact region between the LC phases of compounds **2ET/12** and **2ET/14** in a certain concentration range there is an isotropic liquid ribbon separating them (see Fig. 3b), and indicating that the two LC phases should have a different structure and thus **2ET/14** cannot form a triangular honeycomb. Because the aromatic core length of the **2ET/n** compounds is exactly the same, there is a matching in the honeycomb wall dimensions of the different compounds, and therefore their honeycomb frames are compatible with each other. For this reason honeycombs with identical polygon shape have a complete miscibility whereas those with different polygon shape cannot mix, and this allows the use of miscibility studies for LC phase assignment of these compounds.

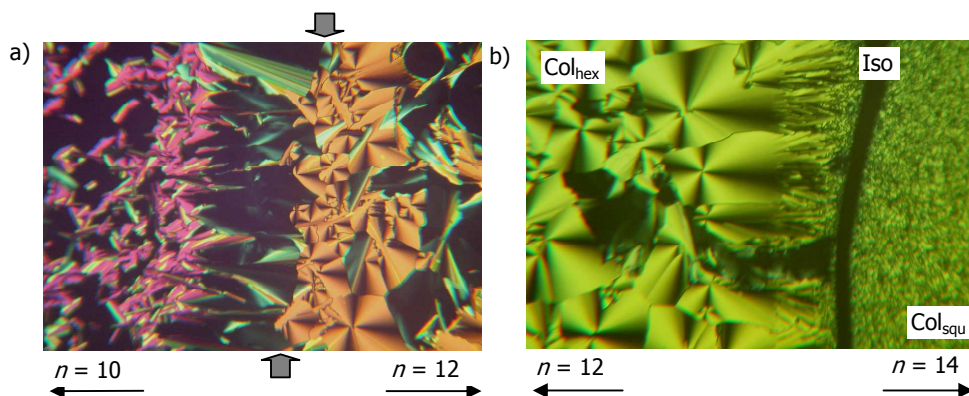


Fig. 3 (a) Contact region between the triangular honeycomb type LC phases of **2ET/10** and **2ET/12** at $T = 84$ °C, arrows indicate the approximate position of the boundary between the two compounds; dark areas represent homeotropically aligned regions of the $\text{Col}_{\text{hex}}\Delta/p6mm$ phases; the development of the contact region is shown in Fig. S3; the reduced birefringence of **2ET/12** compared to **2ET/10** (purple vs. orange) is assumed to be due to a decreased orientational order parameter of the aromatic cores in the honeycomb walls, resulting from the overcrowding of the honeycomb cells by the alkyl chains, occurring before the transition to the square honeycomb structure. The cores are more strictly parallel to the column normal in the Col_{hex} phase of **2ET/10**, whereas for **2ET/12** there is a reduced order parameter of these cores due to

an increased average deviation from being exactly parallel to the column normal. (b) Contact region between the triangular honeycomb of **2ET/12** and the square honeycomb of **2ET/14** at $T = 61$ °C; the isotropic ribbon is an isotropic liquid region observed down to $T \sim 60$ °C, indicating the incompatibility of the two columnar phases with different symmetry.

Indeed, XRD investigations confirm a square columnar phase with $p4mm$ plane group symmetry for **2ET/14** ($\text{Col}_{\text{sq}}/p4mm$), as evident from the ratio of reciprocal spacing $1 : 2^{1/2} : 2$ in the small angle scatterings in the XRD pattern (see Fig. S7 and Table S1). The lattice parameter ($a_{\text{sq}} = 3.15$ nm) is in the range of the molecular length ($L_{\text{mol}} = 3.10\text{--}3.35$ nm), which is in line with a square honeycomb structure for this uniaxial and optical negative mesophase. The same $p4mm$ phase was found for compound **2ET/18** with the longest chains (see Figs. 1g and S8 and Table S1). Figure 1h shows the proposed arrangement of the molecules **2ET/n** ($n = 14, 18$) in the $\text{Col}_{\text{sq}}/p4mm$ phases, where rod-like cores are fused together via hydrogen bonding located at both ends and forming cylinders with square cross sectional area around the lipophilic columns incorporating the lateral alkyl chains. The average number of molecules in the cylinder walls is $n_{\text{wall}} \sim 1.4\text{--}1.5$, which agrees well with the values observed previously for square honeycomb LC phases formed by related compounds (see Table 1).^{18,19,20}

A remarkable feature in the XRD patterns of all $\text{Col}_{\text{hex}}\Delta/p6mm$ phases is the presence of an additional diffuse small angle scattering. This is reproducibly observed, independent on temperature (see Fig. S6 for the diffraction pattern of the supercooled sample of **2ET/10** at $T = 25$ °C), so that it cannot be an artifact due to the coexistence with an isotropic liquid phase as a result of decomposition or any other reason. This kind of diffraction pattern was previously observed for the $\text{Col}_{\text{hex}}\Delta/p6mm$ phases of the related compounds **4/n** ($n = 8, 10$, see Table 1) and interpreted as indication of a defective structure of the triangular honeycombs, actually formed by rhombic cylinders with a time and space averaged random orientation of the rhomb's long axis along the three directions of a hexagonal lattice.^{20,31} This model is in line with the reduced average number of molecules arranged laterally side by side in the cross section of the honeycomb walls (n_{wall}) being only 1.1 to 1.0 for compounds **2ET/10** and **2ET/12**, respectively. Typically, values between 1.3–1.8 were observed for other honeycomb phases of X-shaped bolapolyphiles (see Table 1).¹¹ Thus, besides staggering and lateral side-by-side packing, which shift n_{wall} to larger values, there should also be hole-defects in the walls, shifting n_{wall} to smaller average values. In addition, the decreasing birefringence of the $\text{Col}_{\text{hex}}\Delta/p6mm$ phase upon approaching the limits of its existence range (see contact region between **2ET/10** and **2ET/12** in Fig. 3a) indicates a decreasing order parameter of the π -conjugated cores in the honeycomb walls (larger deviations form an alignment perpendicular to the column long axis), which is in line with the proposed defective structure of these trigonal honeycombs. With growing alkyl chain length hole formation becomes more influential which leads to increasing disorder of the aromatic

cores and hence, the birefringence and the stability of the Col_{hex} phase decrease. Below a critical value of $n_{\text{wall}} \sim 1.0$ the triangular cylinders become unstable, giving way to a square honeycomb at the transition of the alkyl chain length from $n = 12$ to $n = 14$. The square honeycombs have an increased perfection as indicated by the complete absence of any diffuse small angle scattering in the XRD patterns (see Fig. S7).

2.3 Comparison of different series of 2,2'-bithiophene based boalaamphiles

Comparison of the three series of compounds having distinct molecular lengths, namely **2T/n** ($L_{\text{mol}} = 2.9$ nm), **2ET/n** ($L_{\text{mol}} = 3.35$ nm) and **4T/n** ($L_{\text{mol}} = 3.6$ nm; all measured in the same stretched conformation, see Fig. 2), provides additional insights. All three series have similar phase sequences, where, depending on the structure, the distinct phases are shifted towards longer or shorter alkyl chain lengths. The dithiophenes **2T/n** have the lowest phase transition temperatures, which increase in the sequence **2T/n** - **2ET/n** - **4T/n** with the growing length of the rod-like core. This indicates that increasing core length stabilizes the honeycombs. A major contribution to LC phase stability might arise from the growing incompatibility of the longer rigid rods with the flexible alkyl chains, enhancing the phase stability by increasing nano-segregation due to the mainly entropy driven rigid-flexible incompatibility. In the same order **2T/n** - **2ET/n** - **4T/n** there is also a tendency towards higher melting temperatures, though there are exceptions.

The compounds of series **2T/n** show predominantly square cylinder phases ($\text{Col}_{\text{sq}}/p4mm$). Here, the relatively short core unit provides only limited space inside the honeycomb cells and therefore for the chain length $n = 10-14$ only square cells can provide sufficient space. Only for compound **2T/18** with the longest chains ($n = 18$) a $\text{Col}_{\text{hex}}/p6mm$ phase is formed, but in this case it is not a triangular honeycomb phase, but instead a LC honeycomb formed by hexagonal cells with 6 molecules in the circumference of the cells ($\text{Col}_{\text{hex-6}}/p6mm$). Compound **2T/8** with shorter octyl chains does not form any LC phase. So overall, triangular LC honeycombs seem to be unstable for these compounds with relatively short rod-like cores. For compounds **2ET/n** with a longer aromatic core, reported herein, additional space is available in the cylinder cells and therefore there is a tendency to form smaller triangular cylinder cells if the alkyl chain length is $n = 8-12$. Hence, besides the square cylinders also triangular cylinders were observed ($\text{Col}_{\text{hex}\Delta}/p6mm$). On chain elongation the stability of the triangular honeycomb is reduced and after a local minimum between $n = 12$ and 14, further chain elongation leads to square honeycomb phases for $n = 14-18$. For the series of compounds **4T/n** with the longest aromatic cores an even broader variety of LC phases was found, in this case ranging from SmA via $\text{Col}_{\text{hex}\Delta}/p6mm$, $\text{Col}_{\text{sq}}/p4gm$, a nematic phase (N) to $\text{Col}_{\text{sq}}/p4mm$. In this series of compounds, too, there is a local minimum for the mesophase stability

depending on alkyl chain length. This minimum which is associated with a transition from triangular ($p6mm$) to square honeycombs ($p4mm$) is shifted for compounds $4T/n$ a bit to shorter chain lengths compared to the series $2ET/n$ ($n = 12-14$ for $2ET/n$ and $n = 12$ for $4T/n$, even for $n = 12$ there is a low temperature $p4gm$ honeycomb phase comprising squares). This is surprising, because the longer core of $4T/n$ should provide more free space in the cylinder cells and thus should favour the formation of triangular cylinders more strongly than $2ET/n$, i.e. it would be expected that the minimum should be shifted into the opposite direction. That this is not the case can be explained by the smaller average cross section of the aromatic cores involving the slim C-C triple bond compared to the more bulky thiophene ring of $4T/n$. Thus, for compounds $2ET/n$ more space remains available in the cylinder cells to be filled by the alkyl chains, and therefore longer chains are required to fill the square cylinders. On the other hand, the longer rod-like core of $4T/n$ give rise to an increased tendency for parallel alignment of the cores and therefore SmA and nematic phases were observed for compounds $4T/n$, which are missing for the series $2T/n$ and $2ET/n$ with shorter cores (Table 1). In addition, in the case of $2ET/n$ the linear acetylene units at the 2,2'-dithiophene core provide a more pronounced zigzag like overall molecular shape (see Fig. 2) which might additionally contribute to the reduced tendency for orientational order of these cores. Besides these main effects, there could be additional structural effects influencing the mode of self-assembly, as for example the rotational barriers between the individual rings forming the rigid core, which should be very different for compounds $2ET/n$ and $4T/n$, leading to a distinct conformations and overall flexibilities of the core units. Moreover, the conformational freedom of the alkyl chains should be affected by the type of adjacent unit in the 5- and 5'-positions of the 2,2'-dithiophene core and this might affect the mode of chain packing inside the honeycomb cells.

2.4 Luminescent properties

The UV-vis absorption and fluorescence spectroscopic data in $CHCl_3$ solution ($c = 10^{-6}$ mol L^{-1}) and in condensed states are shown in Fig. 4 for compound $2ET/18$ which was chosen to be investigated. This compound shows the maximum absorption peaks at 395 nm, 384 nm and 389 nm in solution, LC state and solid state respectively, which may be attributed to the $\pi-\pi^*$ transitions. The blue shifts (of about 11 nm in LC state and 6 nm in solid state respectively) suggest the formation of π -stacked aggregates with a H-type parallel stacking mode both in LC state and in the solid state.³² The photoluminescence (PL) spectrum of $2ET/18$ in the LC phase and solid state exhibits broad and red-shifted emission with maxima at 517 nm and 513 nm respectively, while the solution displays a structured emission with maxima at 460 nm and 480 nm. Hence, the Stokes shift has a remarkably large value of 124-133 nm in the condensed states (LC state

and solid state) related to 65 nm in CHCl_3 solution, which confirms the strong intramolecular charge transfer in compound **2ET/18**.³³ This feature indicates that these compounds have a significant potential for application in fluorescence sensor³⁴ and photoactive functional assemblies.³⁵

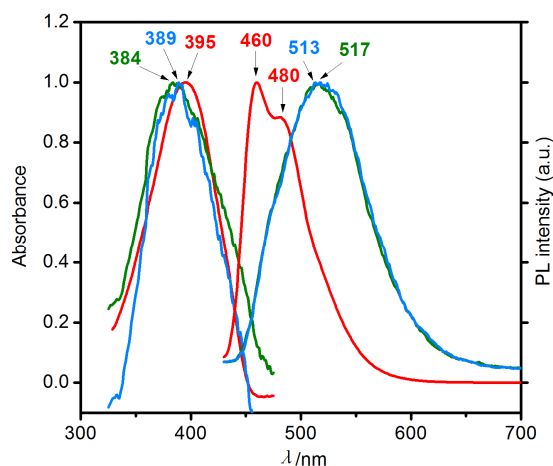


Fig. 4 UV-vis absorption spectra (left) and photoluminescence spectra (right) of compound **2ET/18** in CHCl_3 solution (10^{-6} M) (red line), liquid crystalline state at 35 °C (green line) and solid thin film (blue line).

3. Conclusion

In summary, a series of novel X-shaped bolapolyphiles incorporating a rigid and fluorescence active 5,5'-bis(phenylethynyl)-2,2'-bithiophene core with glycerol groups at both ends and two lateral alkyl chains was synthesized through a straightforward synthesis pathway. By elongation of the lateral alkyl chains, a transition from defective triangular to square honeycomb LCs, separated by a local minimum of the LC phase stability was observed. This indicates that the additional triple bonds, though enabling the formation of triangular cylinders, obviously do not provide that degree of core elongation as would be required for the occurrence of additional intermediate phases combining triangles and squares in a common superstructure, which would be required to give rise to larger superlattice structures, eventually leading to quasi-periodic columnar LC phases.

4. Experimental

^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 solution on a Bruker-DRX-500 spectrometer with tetramethylsilane (TMS) as the internal standard. Elemental analysis was performed using an Elementar VARIO EL elemental analyzer. A Mettler heating stage (FP 82 HT) was used for polarizing optical microscopy (POM, Optiphot 2, Nikon) and DSCs were recorded with a DSC-7 calorimeter (PerkinElmer) at 10 K min^{-1} . X-Ray diffraction (XRD) of surface aligned samples was performed using a 2D-detector (HI-Star, Siemens or Vantec-500, Bruker). Ni filtered and pin hole collimated CuK_α was used. Details of synthesis, purification and analytical data are reported in the SI.

Acknowledgment

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Graphical Abstract

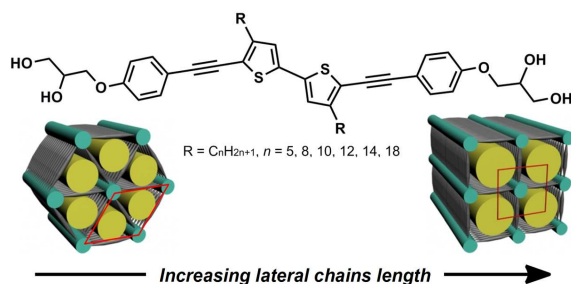
Synthesis and self-assembly of 5,5'-Bis(phenylethynyl)-2,2'-bithiophene-based Bolapolyphiles in triangular and square liquid crystalline honeycombs[†]

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A series of X-shaped bolapolyphiles based on a luminescent π -conjugated core forms nano-structured fluids with triangular or square honeycomb structure.