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Heterolithic azobenzene-containing supermolecular tripedal liquid crystals self-organizing into highly segregated bilayered smectic phases[†]

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Synthesis, self-organization, and optical properties of supermolecular tripedal liquid crystals incorporating various prototypical mesogenic units such as alkoxy-azobenzene (AZB), alkoxybiphenylene (BPH) or alkoxy-cyanobiphenyl (OCB) derivatives are reported. Different molecular systems were designed in order to sequentially incorporate the smectogenic-like alkoxy-azobenzenebased chromophore within the molecular structure, whose relative proportion is selectively varied by exchanging with the other mesogens. A divergent synthetic mode was elaborated for their synthesis, starting from the regioselective functionalization of the phloroglucinol-based (PG) inner core. This methodology allowed the preparation of several sets of unconventional tripedal oligomers with conjugated heterolithic structures (made of different blocks, e.g. $PG_6AZB_xBPH_{3-x}$ and $PG_6AZB_xOCB_{3-x}$, x = 1 or 2) along the homolithic parents (all identical blocks, e.g. PG_zAZB_3 , z = 6or 11, z is the number of methylene in the spacer between PG and the protomesogen, PG_6BPH_3 , and PG₆OCB₃), respectively. Essentially all the synthesized systems behave as thermotropic liquid crystals and show various types of highly segregated multilayered smectic phases, or, in one case, a nematic phase, depending on the nature of the constitutive anisotropic blocks and on the molecular topology (homolithic versus heterolithic, mesogenic ratio x : 3 - x). The effects of these structural modifications on the mesomorphism (mesophase structures, temperature ranges, and thermodynamic stability) have been investigated by differential scanning calorimetry and small-angle X-ray diffraction experiments combined with dilatometric measurements. Models describing the various supramolecular organizations of these tripedes into such multilayered structures are proposed and discussed. Preliminary results of the investigations of their optical properties will also be presented.

1. Introduction

Supramolecular chemistry is a powerful tool to elaborate preprogrammed self-assemblies of single molecules, interacting by non-covalent intermolecular forces and specific molecular recognition criterion, into highly complex and exquisite functional networks mimicking living systems of interest in life and material sciences.¹ Among the diversity of materials able to selfassemble into ordered supramolecular edifices, liquid-crystalline

(LCs) materials continuously emerge as prime candidates due to their dynamic nature, function-integration and stimuli-responsiveness.² This class of soft materials which combines order with fluidity within various types of mobile and low-dimensional periodic structures seems indeed suited in the future development of organic-based organization-dependent technological (e.g. optic- and electronic-based) and biological (molecular machines, guest-host systems, sensors, catalysts, switches, signal amplification devices, therapeutic and transfecting agents, etc.) applications.³ Moreover, the properties of the single molecules can be transferred and considerably enhanced within ordered supramolecular soft assemblies and occasionally even new properties and functions may emerge.⁴ The judicious choice and careful molecular design of the primary constitutive building blocks (chemical shape, interaction strength, specificity and directionality) permit us to partially predict the nature of such dynamic supramolecular assemblies, although the strict control of selfassembling and self-organizing processes and the function transfer from nano- to micrometric scale by molecular engineering still remain challenging.

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The majority of low-molecular weight thermotropic mesogens possesses a prototypical molecular structure made of at least two segments with contrasting chemical or structural character (amphiphilicity),⁵ most often a rigid anisometric core, e.g. with a rod-like or a disk-like shape, equipped with flexible alkyl or perfluorinated end-chains.² Such a straightforward design usually lends to nematic and/or smectic phases for the former and to columnar mesophases for the latter. The discovery that other types of amphipathic molecules based on different structural paradigms, such as those made of a bent core⁶ or with poliphilic T- and X-shaped^{7,8} architectures, was also compatible with mesomorphism (generation of new families of LC phases e.g. polar phases⁶ and polygonal honeycombs,^{7,8} respectively), revived considerable interest in the design of molecules for preprogrammed self-assemblies with increasing complexity.9 Alternatively, driven by the need to expand further the range of mesomorphic organizations and to develop original and multifunctional materials, oligomeric molecular systems, with perfectly controlled geometry (symmetrical or not) and identifiable molecular sub-units, have also been considered as potentially interesting candidates.¹⁰⁻¹³ In addition to their intrinsic advantages, such intricate molecular systems, which combine traits of discrete low-molecular-weight materials (monodisperse) with those of polymers (various degrees of conformational flexibility, size-modulated viscosity, glass transition, etc.), represent indeed an attractive way of adding functionality (e.g., multifunctional and high control of functionality specificity and hierarchy) and in designing "multitask materials" with tunable properties (combination of properties of the inserted molecular species, induction of cooperative and synergistic behavior by selforganization).14 The basic structure of these functional supermolecules usually consists of protomesogenic units linked together through flexible spacers (alkyl, siloxane chains, etc.) to generate linear oligomeric systems, ^{10,11,14} or alternatively via a central focal multivalent node to yield molecular structures with branched architectures such as polypedes¹² and dendrimers.¹³ The structural diversity offered by such supermolecular LCs (connectivity, topology, restricted flexibility) is translated into the nature of the supramolecular organizations formed which often present unusual morphologies induced by the segregation at the molecular level between the various building species.¹⁰⁻¹⁴

For this study, unconventional liquid-crystalline tripedal molecular systems with homogeneous and heterogeneous structures were synthesized. A specific divergent synthesis was elaborated in order to selectively incorporate the protomesogenic alkoxy-azobenzene-based chromophore within the supermolecular structure. As such, the relative proportion between alkoxy-azobenzene (AZB) and alkoxy-biphenylene (BPH) or alkoxy-cyanobiphenyl (OCB) mesogens, respectively, could be varied stepwise in a controlled manner. Thus, this synthetic methodology afforded the preparation of several sets of phloroglucinol (PG)-based tripedal oligomers with homolithic (all identical blocks, e.g. PG₁₁AZB₃, PG₆AZB₃, PG_6BPH_3 , and PG_6OCB_3) and conjugated heterolithic (different blocks, e.g. $PG_6AZB_xBPH_{3-x}$ and $PG_6AZB_xOCB_{3-x}$) structures, respectively.15 Essentially all compounds are mesomorphic (except PG_6BPH_3), and the mesophase structures have been thoroughly investigated by small-angle X-ray diffraction. In particular, bilayered SmC- or SmA-like mesophases were

generated in the heterolithic systems. The effects of the nature of the constitutive anisotropic blocks (AZB, BPH, OCB) and the molecular topology (homolithic *versus* heterolithic, mesogenic ratio x: 3 - x) on the mesomorphism (mesophase structures and stability) are discussed and models describing the various supramolecular organizations into such multilayer structures are presented. Preliminary investigations of their optical properties are also given.

2. Results and discussion

2.1. Design and synthesis

The various homolithic and heterolithic phloroglucinol-based (PG)trimeric materials, hereafter abbreviated as $PG_zAZB_xBPH_{3-x}$ or $PG_zAZB_xOCB_{3-x}$, where z = 6 or 11 is the number of methylene units within the alkyl spacer between PG and the peripheral mesogenic units, were prepared by a divergent protocol involving the repetition of etherification reactions from phloroglucinol (homogeneous PG₁₁AZB₃ trimer) or hydroxyl protected phloroglucinol (PG₆-based trimers). The mesogenic units e.g. 4-alkoxy-azobenzene (AZB), 4-alkoxy-biphenyl (BPH) and 4-alkoxy-cyanobiphenyl (OCB) based-groups were chosen for their specific molecular structures, easy synthetic access and tendency to form liquid-crystalline mesophases.² In order to tune and eventually compare both mesomorphic and optical properties of these materials, the AZB/BPH or AZB/OCB ratios (x:(3 - x)) were varied within the supermolecular structure according to the sequence $3: 0 \rightarrow 2: 1 \rightarrow 1: 2 \rightarrow 0: 3$.

The synthesis of the two homolithic trimers incorporating azobenzene functional groups, PG₆AZB₃ and PG₁₁AZB₃, was carried out according to two different protocols. The divergent synthesis of PG₁₁AZB₃ was achieved in two steps by the complete etherification of phloroglucinol from the commercially available 11-bromo-1-undecanol via Mitsunobu reaction, and the subsequent Williamson etherification of the resulting tribromide derivative (1) with 4-hydroxy-4'-(undecyloxy)azobenzene (2), prepared beforehand (Scheme 1). The synthesis of PG₆AZB₃ was also performed by a divergent procedure but involved the preparation of the difunctionalized intermediate "PG₆AZB₂OH" (5), as a useful precursor for the synthesis of the corresponding mixed materials (PG₆AZB₂BPH, PG₆AZB₂OCB, vide infra, Scheme 2). This procedure included firstly the double etherification of 3,5dihydroxyphenyl benzoate (3) by 6-bromo-1-hexanol via Mitsunobu reaction, the etherification of the end-bromide derivative (4) with 4-hydroxy-4'-(undecyloxy)azobenzene (2), followed by the hydrolysis of the protecting benzoate group to lead to the hydroxyl PG derivative (5). Then, in the second stage, the ether coupling of PG₆AZB₂OH with excess of 1,6dibromohexane resulted in the bromide derivative (6), and the subsequent etherification with (2) provided the homogeneous trimer PG₆AZB₃ (Scheme 1).

The heterogeneous trimers PG_6AZB_2BPH and PG_6AZB_2OCB were directly obtained in a one step procedure by etherification of the intermediate phenolic derivative PG_6AZB_2OH (5) and the corresponding mesogenic brominated monomers 4-(6-bromohexyloxy)-4'-(hexyloxy)biphenyl (8) and 4'-(6-bromohexyloxy) biphenyl-4-carbonitrile (10), previously synthesized according to





Scheme 1 Synthesis of homolithic PG_zAZB_3 . *Reagents and conditions*: (i): DIAD, PPh₃, THF, 0 °C to reflux; (ii): K_2CO_3 , DMF, 90 °C; (iii): KOH, THF–H₂O, reflux.

standard procedures starting from 4'-(hexyloxy)biphenyl-4-ol (7) and 4'-hydroxybiphenyl-4-carbonitrile (9), respectively (Scheme 2).

The mixed conjugates *i.e.* PG_6BPH_2AZB and PG_6OCB_2AZB , were prepared similarly by ether coupling of 4-(6-bromohexyloxy)-4'-(hexyloxy)azobenzene (11) with the phenolic derivatives, PG_6BPH_2OH (12) and PG_6OCB_2OH (13), respectively (Scheme 2). These two phenolic derivatives were obtained from the ether coupling of monoprotected PG (3) with the bromide derivatives (8) and (10), respectively, followed by hydrolysis. During these syntheses, two by-products were formed *in situ*, likely due to the simultaneous deprotection of the 3,5-dihydroxyphenyl benzoate, which were isolated as the two homogeneous PG_6BPH_3 and PG_6OCB_3 compounds, respectively.

All the synthetic details are given in the Experimental section of the ESI.[†] The structure of all materials was confirmed by ¹H and ¹³C NMR. The purity and the structure of the eight final products (PG₁₁AZB₃, PG₆AZB₃, PG₆BPH₃, PG₆OCB₃, PG₆BPH₂AZB, PG₆OCB₂AZB, PG₆AZB₂BPH and PG₆AZ-B₂OCB) were further confirmed by additional Mass Spectroscopy (MALDI-TOF) and C, H, N elemental analysis.

2.2. Thermal behavior and liquid-crystalline properties

The thermal behaviour of the various phloroglucinol-based derivatives was investigated by TGA, DSC, POM and SA-XRD, and is summarized in the table below (Table 1). All compounds



Scheme 2 Synthesis of the heterolithic (PG₆AZB₂BPH, PG₆AZB₂OCB PG₆BPH₂AZB and PG₆OCB₂AZB) and homolithic (PG₆BPH₃ and PG₆OCB₃) compounds. *Reagents and conditions*: (i) K₂CO₃, acetone, 50 °C; (ii) K₂CO₃, KI, 18 crown-6, solvent (DMF: 80 °C, or acetone: 50 °C, or THF: 65 °C, or DMF–THF: 65 °C); (iii) KOH, THF–H₂O, reflux.

are stable above 300 °C and exhibit similar decomposition pathways, except $PG_{11}AZB_3$, which starts degrading just above 200 °C (ESI[†]).

The two homolithic azobenzene derivatives (PG₆AZB₃ and $PG_{11}AZB_3$) are mesomorphic, although the phase domain is strongly reduced when the spacer chain-length is shortened: $PG_{11}AZB_3$ shows a mesophase between *ca.* 100 and 120 °C, whereas the phase becomes monotropic for the shortest homologue (PG_6AZB_3). This is the result of the decrease of the melting temperature for the longer spacer, the mesophase-to-isotropic phase transition temperatures remaining unchanged for both compounds (Table 1). The texture of the enantiotropic phase, shown in Fig. 1, is characteristic of a tilted disordered SmC phase as identified by the presence of Schlieren features and striated domains.16 The monotropic phase was harder to detect due to its short temperature range (about 3 °C only on cooling), and could not be unequivocally assigned. At the isotropic-to-mesophase temperature transition, the furtive formation of small focal conics was sufficient to assign the formation of a SmC phase too.

Diffraction patterns of PG₁₁AZB₃ recorded between 105 and 120 °C confirmed the LC nature of the mesophase. The diffractogram registered at 110 °C, described as a representative example (Fig. 2), shows a sharp and intense small-angle reflection whose position gives a periodicity of 37.25 Å (d_{001}), along the presence of a large and diffuse signal at *ca.* 4.5 Å associated with the liquid-like lateral ordering of the molten chains and mesogenic cores ($h_{ch} + h_c$). This, along with POM observation, permits the unequivocal assignment of the mesophase as SmC. Despite its narrow domain of existence, a diffraction pattern of

Table 1 Phase transition temperatures (°C) and corresponding enthalpy ΔH (J g⁻¹) or specific heat variation ΔCp (J g⁻¹ °C⁻¹)^{*a,b*}

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PG<sub>11</sub>AZB<sub>3</sub>
LamCr 100.3 (-) LamCr' 107.2 (83.9)<sup>c</sup> SmC 120.5 (21.2) I
I 121.4 (-25.4) SmC 90.8 (-) LamCr' 78.5 (-48.4)<sup>c</sup> LamCr
LamCr 100.4 (50.9) SmC 120.7 (22.1) I
PG<sub>6</sub>AZB<sub>3</sub>
LamCr 66.0 (8.5) LamCr' 87.9 (1.01) LamCr" 123.7 (48.0) I
I 121.0 (-) SmC 118.0 (-58.7)<sup>c</sup> LamCr'' 79.5 (-0.4) LamCr' 63.3 (-2.5) LamCr
LamCr 70.6 (10.2) LamCr' 123.9 (55.6) I
PG<sub>6</sub>AZB<sub>2</sub>BPH
LamCr 76.6 (14.6) LamCr' 108.3 (37.0)<sup>c</sup> SmC 116.0 (-) I
I 115.8 (-13.9) SmC 81.8 (-8.0) LamCr'
LamCr 75.3 (3.2) Cr 84.6 (-9.8) Cr' 108.6 (37.4)<sup>c</sup> SmC 118 (-) I
PG<sub>6</sub>BPH<sub>2</sub>AZB
LamCr 119.3 (64.7) I
I 118 (-31.3) SmC 101.9 (-31.1) LamCr
PG<sub>6</sub>BPH<sub>3</sub>
LamCr 147.3 (76.7) I
I 130.3 (-76.0) LamCr
PG<sub>6</sub>AZB<sub>2</sub>OCB
Cr 105.0 (6.4) Cr' 116.0 (57.8) SmA 122.8 (12.8) I
I 124.8 (-12.9) SmA 9.8 (0.25) G
G 17.4 (0.28) SmA 42.5 (-4.4) Cr 66.8 (4.6) Cr' 70.0 (-24.0) Cr'' 103.7 (19.3) Cr''' 108.0 (-24.9) Cr''' 114.2 (26.6) SmA 123.5 (11.42) I
PG<sub>6</sub>OCB<sub>2</sub>AZB
Cr 55.9 (24.8) Cr' 62.0 (-28.3) Cr' 91.2 (37.4) SmA 116.0 (9.2) I
I 117.1 (-9.2) SmA 3.6 (0.43) G
G 7.4 (0.45) SmA 116.2 (9.8) I
PG<sub>6</sub>OCB<sub>3</sub>
Cr 133.6 (67.0) I
I 108.8 (-3.9) N 18.2 (0.4) G
G 21.8 (0.4) N 108.4 (2.7) I
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^{*a*} Onset temperature (DSC), Cr–Cr''': crystalline phases, LamCr–LamCr'': lamellar crystalline phases, G: glassy state, SmA/C: smectic A/C phases, N: nematic phase, and I: isotropic liquid. ^{*b*} First heating, first cooling, and second heating. ^{*c*} Cumulated enthalpy.



Fig. 1 Polarized optical microphotographs of the LC trimers, observed on cooling from the isotropic liquid state. Clockwise from top left: $PG_{11}AZB_3$ (SmC, T = 116 °C), PG_6AZB_2BPH (SmC, T = 112 °C), PG_6AZB_2OCB (SmA, T = 117 °C), and PG_6OCB_3 (N, T = 70 °C).

the monotropic mesophase (PG₆AZB₃) could luckily be obtained at 120 °C, in the vicinity of the isotropic liquid: it revealed a single small-angle reflection corresponding to the lamellar periodicity ($d_{001} \approx 60.9$ Å). For both compounds, the SmC mesophase transforms on further cooling into crystalline phases with a highly pronounced layered character and sharp interfaces as testified by XRD, thereafter labelled as LamCr phases. Patterns



Fig. 2 Representative small-angle X-ray patterns of $PG_{11}AZB_3$ (SmC, 100 °C) and PG_6AZB_2BPH (SmC, 100 °C).

measured down to room temperature systematically revealed up to four sharp small-angle reflections in the ratio 1:2:3:4 and the occurrence of several sharp large-angle peaks (three to five)

Table 2 Structural parameters of the mesophases^a

Compounds	d /Å, $N_{\rm L}$, $n_{\rm Lmesi}$	$V_{\rm mol}/{\rm \AA}^3, A_{\rm mol}/{\rm \AA}^2, n_{\rm Amesi}$	$a_{\text{AZB}}/\text{\AA}^2$, $(a_{\text{BPH}}/a_{\text{OCB}})$	$d_{\text{AZB}}/\text{\AA}, (d_{\text{BPH}}/d_{\text{OCB}})$	$\psi_{AZB}^{\circ}, \ (\psi_{BPH}/\psi_{OCB})$
$PG_{11}AZB_3$, SmC ($T = 110 \ ^{\circ}C$)	37.2, 1, 1	2820, 75.7, 3	25.2, (-)	10.95, (-)	≈25, (-)
PG_6AZB_3 , SmC ($T = 120$ °C)	60.9, 2, 2	2405, 39.5, 1.5	26.3, (-)	10.6, (-)	$\approx 30, (-)$
PG_6AZB_2BPH , SmC ($T = 100$ °C)	55.1, 2, 1 : 1	2196, 39.9, 2 : 1	20.0, (40.0)	13.8, 6.1	$0, (\approx 55)$
PG_6BPH_2AZB , $SmC(T = 115 °C)$	51.2, 2, 1 : 1	2043, 39.9, 1 : 2	40.0, (20.0)	6.95, (12.3)	≈ 55, (0)
$PG_{6}AZB_{2}OCB$, SmA ($T = 114 \degree C$)	30.8, 1, 1 : 1	2062, 67.1, [2 + 1]	22.5, (22.5)	[12.2]	0, (0)
PG_6OCB_2AZB , SmA ($T = 102 \circ C$)	28.8, 1, 1 : 1	1715, 59.7, [1 + 2]	22.5, (18.5)*	[13.3]	0, (0)*
^{<i>a</i>} <i>d</i> is the smectic periodicity, $N_{\rm L}$ is th number of sub-layers containing the	e number of mesog mesogenic groups o	enic layers per smectic period of type i (i = AZB, BPH or 0	d ($N_{\rm L} = 1$ for a monolaye OCB) in a smectic layer, V	r and $N_{\rm L} = 2$ for a bilaye $N_{\rm mol}$ is the molecular volu	er), n_{Lmesi} is the me, A_{mol} is the

number of sub-layers containing the mesogenic groups of type i (i = AZB, BPH or OCB) in a smectic layer, V_{mol} is the molecular volume, A_{mol} is the number of mesogenic groups of type i covering the area A_{mol} in sub-layers [for OCB-containing trimers, mesogen sublayers are not differentiated and thus appear constituted by both mesogens, see text], a_i is the mesogenic area, $a_i = A_{mol}/n_{Amesi}$ (*calculated for a monolayer OCB packing, but the small value reveals a change of the packing type, see text), d_i is the sub-layer thickness $d_i = f_i \times d/n_{Lmesi}$ [average thickness deduced from the sum of both mesogens' volume fractions, f_i (ESI†)], ψ is the tilt angle, $\psi = \arccos(\sigma/a_i) = \arccos(d_i/l_i)$ with $\sigma \approx V_{CH_2}/1.27$ and $l_{AZB} \approx 12.2$, $l_{PBH} \approx 10.8$, $l_{OCB} \approx 11.5$ Å.

rising indicative of the chain crystallization and 3D crystalline packing.

The sequential exchange of azobenzene by biphenylene groups along the series $PG_6AZB_3 \rightarrow PG_6AZB_2BPH \rightarrow PG_6BPH_2AZB$ \rightarrow PG₆BPH₃ does not modify significantly the liquid crystalline properties, and in particular the SmC-to-I transition temperature is almost constant for all AZB-containing compounds (Table 1). However, for both heterolithic systems the melting temperatures are depressed by 13 and 20 °C with respect to ideal mixtures of similar composition for PG₆AZB₂BPH and PG₆BPH₂AZB, respectively. Such a thermal behaviour (of the heterolithic compounds) resembles that associated with eutectic solid phases' macrosegregation in mixtures,¹⁷ although here the two components can only microsegregate at the molecular level in alternating sub-layers since they are chemically connected. As for technically used liquid crystal mixtures, this melting point depression, conjugated to a quite ideal clearing temperature variation (here between 116 and 121 °C, Table 1), logically leads to mesophase induction at intermediate compositions. Thus, both heterolithic tripedes show the smectic C phase on a broader range than PG₆AZB₃, whereas mesomorphism is not observed in the homolithic biphenylene-containing compound (PG₆BPH₃): PG₆AZB₂BPH exhibits an enantiotropic domain (ca. 10 °C on heating) which can be supercooled (e.g. down to ca. 80 °C), whilst the mesophase is monotropic by only 1 °C for the conjugate homolog.

The SmC phase was confirmed by the observation of typical Schlieren textures (Fig. 1) and by XRD (Fig. 2). Diffraction patterns recorded for PG₆AZB₂BPH between 115 and down to 85 °C are all identical: they display two intense, sharp, small-angle reflections in the ratio 1 : 2, indexed as $d_{001} = 55.1$ for the most intense, and $d_{002} = 27.55$ Å for the second order, characteristic of the layering of the molecular arrangement, and the diffuse scattering corresponding to the molten chains and mesogenic cores (Table 2). The abnormal intensity profile in the reflection series, with a relatively intense (002) reflection with respect to (001), indicates segregation at the molecular level, with alternation of several high-electronic density sub-layers, respectively, associated with two different mesogens, with low-electronic density sublayers, associated with the aliphatic tails and with the alkyl spacers (*vide infra*, Fig. 4). The respective

intensities of first and second order reflections then depend on a subtle manner from the respective thickness ratios of these sublayers, from the electronic density increase within aliphatic sublayers due to PG nodes and from the sharpness of their interfaces, *i.e.* the quality of the segregation between mesogens and aliphatic parts. A different intensity ratio may thus be expected for PG₆BPH₂AZB, having an opposite number of undecyl and hexyl terminal chains, and therefore a different sublayer thickness ratio. Unfortunately, such a quantitative comparison (first-to-second order intensity-ratio) could not be performed since only one reflection of low intensity was detected $(d_{001} = 51.2 \text{ Å})$ in this case, during the substantially shortened acquisition, due to the mesophase metastability (monotropic SmC). As for the pure azobenzene derivatives, both heterolithic compounds form low-temperature crystalline phases with a pronounced layering, as evidenced by XRD (LamCr).

The same melting temperature decrease is also observed when the azobenzene units are sequentially exchanged by the stronger cyanobiphenyl mesomorphic promoter along the series $PG_6AZB_3 \rightarrow PG_6AZB_2OCB \rightarrow PG_6OCB_2AZB \rightarrow PG_6OCB_3.$ However, discrepancy from ideality is much larger here, expected due to the different chemical structures of both constitutive mesogens (AZB and OCB). Consequently, the induction of mesomorphism is also larger in this series. For instance, the depression is around 11 °C for the low OCB-content trimer PG₆AZB₂OCB and reaches even 40 °C for PG₆OCB₂AZB, giving rise to enantiotropic mesophase domains of 7 and 25 °C, respectively. In contrast, mesophases of both homolithic compounds are monotropic. Nevertheless, for all the OCB-containing compounds, the mesophases can be supercooled and frozen into a glassy state close to room-temperature (DSC, ESI[†]). It should be noted that the thermal behaviour of the low OCB-content trimer is, however, not fully reversible on subsequent heating and exhibits a complicated thermal behaviour with a succession of crystallization and melting events. In contrast to the previous system, $PG_zAZB_xBPH_{3-x}$, the mesophase exhibited by both heterolithic compounds is different from that of both homolithic compounds: thus, at both extremes, SmC (for PG₆AZB₃) and N (for PG₆OCB₃, Fig. 1) phases are present, whilst a SmA mesophase was induced in both intermediate compounds, readily identified by POM (Fig. 1, ESI⁺). It is noteworthy that the behaviour exhibited in this series reproduces the typical behaviour of classical calamitic mesogens within homologous series, with the N phase observed at the short chainlength, the SmC phase at the longer chain-length, and the SmA phase at the intermediate chain-length.¹⁸ X-ray patterns of both samples confirm the smectic nature of the mesophase, and show only one sharp small-angle reflection along the broad and diffuse scattering in the wide-angle range ($h_{ch} + h_c$, Fig. 3): layer periodicities are of the order of 30 Å (Table 2) and no appreciable variation of the *d*-spacing with temperature signifies the absence of significant tilt angle variations.

2.3. Self-organization properties

The mesogens involved in these compound series are typical calamitic smectogens, therefore smectic mesomorphism was expected. However, due to the specific tripedal architecture and nodes, the conformational freedom is reduced, and thus the layering is substantially constrained. Indeed, the homolothic tripedes are not liquid-crystalline or show only monotropic behaviour, but quite remarkably mesomorphism was promoted in the heterolithic tripedes. As shown above, this promotion is actually due to the depression of the melting points associated with the co-crystallization of segregating mesogens in separated layers, and not to the clearing point variation, the relative deviation from ideality being rather modest. Despite the complexity introduced by the additional segregation between mesogens due to 2:1 stoichiometry in heterolithic systems (which does not occur in homolothic compounds), the accommodation of the different sub-layer areas can take place according to different processes as listed below (Fig. 4):

(i) intimate mixing of incompatible mesogens within one single sub-layer alternating with either sub-layers of mixed tails, spacers and nodes (case a), or with differentiated aliphatic sub-layers (case b),

(ii) micro-segregation of the mesogens in alternated layers (AB-type bilayer) either with a large tilt within the sub-layers of the mesogens in minority (case a), or with a strong curvature of the sub-layer interfaces, and a possible evolution toward an alternative type of packings (case b),

(iii) and finally a segregation of the mesogens into a three-layer arrangement of the ABB-type.

The latter ABB arrangement (iii) is excluded by X-ray data: the layer periodicities and the intensity modulation of the lamellar reflection series are compatible with either single or bilayer structures only (Table 2).¹⁵

Since the mesogens are all identical, the mixture of mesogens in one layer trivially occurs for PG₁₁AZB₃ only, likely because the length of the terminal chains and spacer are identical, allowing inter-lamellar exchange without affecting aliphatic sub-layer thickness (Fig. 4(ia)), and with the threefold nodes randomly distributed in those sub-layers: the supramolecular arrangement results of the simple alternation of mesogenic (AZB moieties are slightly tilted) and aliphatic (tails and spacers undifferentiated) layers (Fig. 4(ia)). This was clearly proven by the absence of a double periodicity in long-time acquisition X-ray patterns and the resulting molecular areas. However, this arrangement is no more valid for the smaller homolithic azobenzene-based compound, as the *d*-spacing corresponds to a periodicity of two mesogenic layers, very likely since tails and spacers, which have different lengths, are forced into identifiable layers of different thicknesses, with an average antiparallel orientation of the nodes (Fig. 4(ib)). In contrast, the embedding mesogenic sub-layers are undifferentiated.



Fig. 3 Representative small-angle X-ray patterns of PG_6AZB_2OCB (SmA, 114 °C) and PG_6OCB_2AZB (SmA, 102 °C).



Fig. 4 Possible processes of trimers packing in smectic phases (d_{001} : smectic phase periodicity and the blue line is the corresponding schematic electronic density variation). Top row (from left to right): cases (ia, ib and iii) (not observed here). Bottom row (from left to right): cases (iia and iib). For the homolithic systems PG₁₁AZB₃ and PG₆AZB₃, one-colour brick for ia and ib (see text).

For the heterolithic BPH-containing systems, segregation between the two types of mesogens occurs, leading to a more intricate organization as for the latter, with an additional differentiation between two mesogenic sub-layers (Fig. 4(iia)). Both conjugates give rise to bi-layered organizations with a very high tilt-angle of the low-content component, segregating in a SmC-like sub-layer from non-tilted SmA-like sub-layers of the high-content component. Indeed, the molecular area, identical for both systems, is imposed by the cross-section sum of the highcontent mesogen (Table 2). Nevertheless, the slight loss in the molecular area values (10% smaller compared to the estimated cross-section, $\approx \sigma_{CH_2} \approx 22.5 \text{ Å}^2$, Table 2) suggests that a restricted amount of inter-layer diffusion occurs, simultaneously reducing the tilt angle to 55° (instead of 60° in the ideal case of perfectly segregated mesogens of identical cross-sections).

Unexpectedly, layer-un-differentiation is total for the OCB-containing materials, as evidenced by the monolayer SmA phase (see d and Amol values, Table 2, and also POM, Fig. 1), composed of apparently untilted mesogens mixed in the same layer instead of the bilayer SmC phase formed by the BPH-containing systems just described. Yet, good segregation between the two different mesogens in separated individual layers is a priori expected because of their strong structural difference. In reality, this result is not in contradiction with the occurrence of segregation at the local scale between the mesogens, but the substitution of the alkyl chain by a cyano group reduces the segregation with the aliphatic medium, this hypothesis being supported by the fact that PG₆OCB₃ shows the N phase and not a smectic phase. Therefore, the compensation of the various areas is promoted by a layer undulation process (Fig. 4(iib)) which facilitates permutation between the mesogen sub-layers. At the larger scale-length, this permutation leads to an average apparent sub-layer made of untilted mixed mesogens similar to classical SmA-SmC phases found in calamitic compounds.19 In the particular cases of the OCB-containing systems, the suppression of the terminal chains gives the possibility of a monolayer packing (SmA1) similar to the mesogens with terminal chains, but also to a bi-layer packing (SmA2) through cyano pairing, or to a mixture of both (SmAd).²⁰ The molecular area of the low-OCB content tripede is fully compatible with a SmA1 type, whilst the smaller molecular area of the high-OCB content compound agrees with a SmAd type, with 30 to 40% of pairing.

3. Photochemical behaviour

The photochemical behaviour of the three-armed star-like liquid crystalline molecules containing 1 to 3 photochromic azobenzene groups was investigated. The UV-Vis absorption spectra of such systems in solutions were measured and the photoisomerisation process of azobenzene moieties was studied. Based on these results the light induced anisotropy was investigated in films in the next step.

The UV-Vis spectra of initial and irradiated solutions were recorded, and are characterised by four spectral bands as follows (Fig. 5):

(A) absorption of the aromatic core located below 260 nm;

 (B_1) absorption of the mesogenic alkoxy-biphenyl (BPH) groups at 265 nm (PG₆BPH₂AZB and PG₆AZB₂BPH);

(B₂) absorption of the mesogenic alkoxy-cyanobiphenyl (OCB) groups at 298–302 nm (PG₆AZB₂OCB and PG₆OCB₂AZB);



Fig. 5 UV-Vis spectra of PG_6BPH_2AZB (top) and PG_6OCB_2AZB (bottom) in CHCl₃. Arrows indicate the absorption spectra change after UV (366 nm) light exposure. (A) core band; (B₁) mesogenic BPH band; (B₂) mesogenic OCB band; (C and D) azobenzene bands.

(C) $\pi \rightarrow \pi^*$ transition of the E-form of the azobenzene with a maximum at 360 nm;

(D) $n \rightarrow \pi^*$ transition of the azobenzene at 450 nm.

It is clearly seen that the absorption bands of the azobenzene (C and D) are separated from the mesogen absorption bands (B_1 or B_2). Moreover, it can be noticed that there is a red shift in the alkoxy-cyanobiphenyl absorption bands (B_2) which is caused by the electron acceptor cyano group. Existence of the electron acceptor and electron donor alkoxy groups on biphenyl creates a push–pull effect.²¹

The photoisomerisation process of the azobenzene moiety of PG_6AZB_2BPH in chloroform under UV exposure is shown in Fig. 6. Irradiation at 366 nm results in the photoisomerisation establishing a steady state between the thermodynamically stable E isomeric form of azobenzene and its meta-stable Z-form. As a result, a decrease in the $\pi \rightarrow \pi^*$ absorption between two isosbestic points (322 and 431 nm) and simultaneously an increase in the absorption in the range of the $n \rightarrow \pi^*$ transition (431–490 nm) are observed (Fig. 6). Subsequent Vis exposure (532 nm) results in the establishment of a new steady state rich with E isomers.

The UV-Vis spectra of the other trimeric compounds in solution were similar and variable peak intensities were obtained due to a different proportion of the azobenzene to the mesogenic



Fig. 6 UV-Vis spectra of PG₆AZB₂BPH in CHCl₃ ($C = 2.1 \times 10^{-5}$ mol dm⁻³). Arrows indicate the absorption spectra change after UV (366 nm) light exposure. C and D: azobenzene bands.

Table 3 Absorption maxima (λ_{max}), molar absorption coefficients (ε) of three-arm star-like LC molecules with a different proportion of azobenzenes to mesogens obtained in chloroform at room temperature

$\lambda_{\max} \text{ [nm]} (\varepsilon \text{ [M}^{-1} \text{ cn})$	n ⁻¹])
$\pi \to \pi^*$	$n \rightarrow \pi^*$
360 (73 000)	452 (9000)
360 (76 000)	448 (8700)
360 (30 000)	450 (3500)
360 (46 000)	450 (6000)
360 (61 000)	451 (6800)
360 (29 000)	453 (3300)
	$\frac{\lambda_{\max} \text{ [nm] } (\varepsilon \text{ [M}^{-1} \text{ cn})}{\pi \to \pi^*}$ $\frac{360 (73 \ 000)}{360 \ (76 \ 000)}$ $\frac{360 (30 \ 000)}{360 \ (46 \ 000)}$ $\frac{360 \ (61 \ 000)}{360 \ (29 \ 000)}$

groups (ESI[†]). The absorption maxima (λ_{max}) together with the molar absorption coefficients (ε) for all investigated materials are collected in Table 3.

However, as shown in Fig. 7, the absorption maximum of the $\pi \rightarrow \pi^*$ transition of spin-coated PG₆AZB₂BPH films is significantly blue shifted up to 336 nm when compared to the spectrum in chloroform. Moreover, the bands have an asymmetric shape. Both observations indicate that a high amount of azobenzene groups exist as H-aggregates.²² This phenomenon is caused by head-to-head stacking of the azobenzene moieties probably promoted by further intra-/intermolecular interactions especially by the van der Waals forces of the terminal tails. In contrast PG₆AZB₂OCB and PG₆OCB₂AZB show a much smaller blue shift of only 5 nm. Based on the results of photo-isomerisation in solution the suitable wavelength of the light was selected for induction of optical anisotropy in films.

The photoisomerisation of azobenzene occurs also in films (Fig. 8). In contrast to the solution, the steady state of the aggregated films is characterized by much less formed Z isomers. The reversibility of photoisomerisation can be used as a light driven motor for the molecular motion in films. The irradiation at the appropriate wavelengths which both isomers absorb results in a number of E–Z and Z–E photoisomerisation cycles. As shown in many studies, the linearly polarized exposure can cause an orientation of the azobenzene groups. The azobenzene chromophores oriented parallel to the electric field vector of the incident light undergo preferably a multiple photoisomerisation cycle up to a situation in which mobile azobenzene moieties become oriented in the direction perpendicular to the light electric field vector, thus optical anisotropy is induced in the film.



Fig. 7 Absorption spectra of PG₆AZB₂BPH in chloroform solution (green-dashed line) and in the film (black-solid line) with the maximum of $\pi \rightarrow \pi^*$ transition.



Fig. 8 Polarized UV-Vis absorption spectra of the PG_6AZB_2BPH film measured with a beam polarized parallel (red-dashed line) and perpendicular (blue-dashed line) to the polarization direction of the incident beam of an Ar⁺ laser (488 nm, 160 mW cm⁻², 43 min) compared with the initial spectrum (black-solid line).



Fig. 9 Absorption polar diagram plotted for 366 nm for the PG_6AZB_2BPH film before (black-solid line) and after irradiation (red-dashed line) with linear polarized laser light (488 nm, 160 mW cm⁻², 43 min).

The absorption spectra of the initial and irradiated PG_6AZB_2BPH films are depicted in Fig. 9. Polarized measurements indicate a weak anisotropy (dichroism of about D = 0.13) with the absorption maximum perpendicular to the electric field vector of the incident light. The spectroscopy revealed that the amount of chromophores oriented in the direction to field vector has been decreased while no increase is observed in the direction perpendicular to the electric field vector of incident light (Fig. 9). Such changes suggest that the orientation process is more complex and contains probably an out-of-plane orientation component of the mobile non-aggregated molecules in the film. The $\pi \to \pi^*$ maximum at 366 nm is not shifted by the exposure indicating that the film is still strongly aggregated. The anisotropy did not increase due to subsequent annealing of films of the LC derivatives.

4. Conclusions

New supermolecular tripedal homo- and heterolithic liquid crystals have been synthesized. Smectic mesomorphism is observed in most compounds as expected since the building blocks are typical calamitic smectogens. Depending on the molecular topology, SmC- or SmA-like phases with monolayer (PG₁₁AZB₃) or bilayer structures were formed. For the heterolithic systems, segregation between the two types of mesogens occurs, leading to more intricate organizations than for the homolithic ones, with a good differentiation between the two mesogenic sub-layers. These various smectic organizations were comprehensively described by the help of classical concepts, such as partial molecular volumes and transverse cross-sections of molecular segments applied at all interfaces generated by the tripedal architecture. A comparison of the UV-Vis spectra of tripedal star-like azobenzene functionalized derivatives in the solution and in spin-coated films revealed a strong "blue" shift of the maximum absorption band indicating the formation of H-aggregates. The aggregated azobenzenes however do not undergo photo-isomerisation nor photo-orientation upon linearly polarized exposure. Consequently, only a small dichroism was induced by light. More detailed optical investigations of the heterolithic derivatives of this series will be presented in a subsequent publication.

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