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# Functional star-shaped tris(triazolyl)triazines: columnar liquid crystal, fluorescent, solvatofluorochromic and electrochemical properties<sup>†</sup>

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Columnar liquid crystals with a  $C_3$  star-shaped heteroaromatic nitrogen-rich core, *i.e.* 2,4,6-tris(1',2',3'triazol-4'-yl)-1,3,5-triazine (TTT), that show luminescence and solvatofluorochromism, and are also electron-acceptors are described. The core has been extended with polyalkoxybenzoyloxyphenyl groups situated at the 1 position of the 1,2,3-triazole rings to obtain molecules with three, six or nine ndecyloxy chains (series **TB**) or three, six or nine (S)-3,7-dimethyloctyloxy chains (series **TB**\*). The preparation of the target compounds involved a copper-catalysed alkyne-azide cycloaddition (CuAAC) "click chemistry" procedure with a 1,3,5-triazine precursor and aromatic azides and this proved to be a versatile way to functionalise the periphery of the heteroaromatic core. Comparison of these compounds and those bearing polyalkoxyphenyl substituents (series T) has led to a deeper understanding of the self-assembly of the compounds with the TTT core. It was found that they selforganise into columnar mesophases, in which two molecules with a low-symmetry conformation occupy on average a columnar stratum. These molecules tend to adopt a polar conformation instead of the apolar  $C_3$  conformation and arrange in an antiparallel assembly. For some compounds the molecules in this arrangement have enough flexibility to tilt upon lowering temperature or by applying an electric field. Interestingly, the hexagonal columnar arrangement is preserved in a glassy state at room temperature. Furthermore, the mesophases show luminescence in the blue region of the visible spectrum depending on the peripheral substitution and molecular structure. We also report a novel property of TTT compounds (series T, TB and TB\*) as they are able to act as solvatofluorochromic probes, a property that allowed us to estimate the overall polarity of the liquid crystalline medium. An aromatic azide precursor was also found to be mesomorphic and exhibited a monolayer SmA mesophase.

# Introduction

Columnar liquid crystals are a class of soft matter in which molecular units self-organise to form arrays of columnar stacks.<sup>1,2</sup> Organic  $\pi$ -conjugated molecules with columnar mesophases are the subject of intense research as in each individual column the interior can include co-facially stacked aromatic cores surrounded by hydrocarbon chains. This configuration can yield materials with efficient charge or energy transport in organic electronic devices such as organic field-effect transistors (OFETs), photovoltaic solar cells and electroluminescent devices.<sup>3-8</sup>

In this regard, it is of interest to investigate novel molecular structures, with different electronic and optical properties, that can form columnar mesomorphism. Significant effort has been focused on electron-rich cores for which high hole mobilities ("p-type semiconduction", that is, holes are more easily injected than electrons from the electrodes) comparable to amorphous silicon have been achieved.9,10 These structures mainly comprise triphenylenes, phthalocyanines and hexaperihexabenzocoronenes. However, very few of these have been reported to show the electron mobility ("n-type semiconduction", that is, electrons are more easily injected than holes) necessary for the preparation of charge-balanced devices.9,11,12 Azaaromatic cores are candidates for columnar liquid crystals with high electron affinity<sup>13-22</sup> as the replacement of a CH group by nitrogen atoms in the aromatic core of the mesogen is one strategy to obtain low LUMO levels and to bring about n-type semiconducting properties.23,24

Motivated by the design of novel multifunctional materials based on columnar liquid crystals we have focused on star-shaped discotics<sup>25–35</sup> due to their appealing structure and properties,<sup>36</sup> based on the 1,3,5-triazine core. The 1,3,5-triazine ring is

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an electron-accepting unit that is able to form columnar mesophases with appropriate substitution at the 2,4,6-positions.16,22,37-44 We recently reported the synthesis of the unprecedented heteroaromatic nitrogen-rich 2,4,6-tris(1',2',3'triazol-4'-yl)-1,3,5-triazine (TTT) core.45 The synthetic procedure included a one-pot deprotection-cycloaddition reaction, one of the few examples in which the copper-catalysed alkyne-azide cvcloaddition (CuAAC) protocol has been applied to columnar liquid crystals,46,47 and this was the first use of triazine and aromatic azide precursors.45 This method allowed us to obtain multifunctional structures that exhibit very stable liquid crystalline columnar phases and luminescence from systems with high electron affinity. We report here the synthesis and the full characterisation (liquid crystalline, redox and optical properties in solution and in the liquid crystal phase) of novel compounds based on the nitrogen-rich TTT core. The versatility of the synthetic procedure has allowed us to extend the core with polvalkoxybenzoyloxyphenyl groups situated at the 1 position of the 1,2,3-triazole rings to obtain star-shaped molecules with three, six or nine *n*-decyloxy chains (series **TB**) or three, six or nine (S)-3,7-dimethyloctyloxy chains (series **TB**\*) (Scheme 1). The **TB** and TB\* series both have longer side arms (a more marked starshape) than series  $T^{45}$  (Scheme 1). These compounds show a marked tendency to form stable hexagonal columnar mesophases. The self-assembly of both, the T and TB series, is discussed here. It was found that in most cases two molecules selforganise into a columnar stratum and that these molecules tend



Scheme 1 Molecular structures of series TB, TB\* and T.<sup>45</sup> O(S)Cit = (S)-3,7-dimethyloctyloxy. Synthetic procedure for the preparation of TB and TB\*. (a) (i) NaNO<sub>2</sub> (aq), HCl, HOAc, H<sub>2</sub>O and (ii) NaN<sub>3</sub> (aq); (b) polyalkoxybenzoic acids, DCC, DMAP, dichloromethane. (c) Sodium ascorbate, CuSO<sub>4</sub>·5H<sub>2</sub>O, TBAF 1 M in THF, THF/H<sub>2</sub>O.

to adopt a polar conformation, instead of the intuitively expected apolar  $C_3$  conformation, and arrange in an antiparallel assembly. We also report a novel property of tristriazolyltriazine compounds in that they act as a solvatofluorochromic probe, which allowed us to estimate in a qualitative way the overall polarity of the liquid crystalline media.

# **Results and discussion**

# Synthesis

Compounds from series **TB** and **TB**<sup>\*</sup> were synthesised by a copper-catalysed alkyne–azide cycloaddition (CuAAC) "click reaction" in which the trimethylsilyl-protected trialkyne 2,4,6tris[(trimethylsilyl)ethynyl]-1,3,5-triazine reacted with the aromatic azides in "one-pot" procedure. In the reaction the alkyne groups are triply deprotected and made to react *in situ* with the aromatic azides. The reactions were carried out at room temperature and gave the desired products in moderate yields (28–51%) (Scheme 1). The <sup>1</sup>H NMR spectra of the final compounds display one singlet for the proton of the triazole rings at 9.2–9.3 ppm, which is consistent with the formation of 1,4disubstituted-1,2,3-triazole rings. The additional chemical characterisation is available in the ESI<sup>†</sup>. The synthetic procedure, which was designed for the preparation of series **T**,<sup>45</sup> proved to be fully applicable to aromatic azides containing an ester group.

Aromatic azides were obtained by esterification with DCC/DMAP of polyalkoxylated benzoic acids with 4-azidophenol, which was previously prepared by diazotization of 4aminophenol followed by reaction with sodium azide.<sup>48</sup> 4-Azidophenol was successfully esterified under these conditions with yields in the range from 77% to almost quantitative. All characterisation data for the new aromatic azide precursors are available in the ESI<sup>†</sup>.

### Thermal properties. Liquid crystalline properties

Series **TB** and **TB**<sup>\*</sup> were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and polarised optical microscopy (POM). The liquid crystalline properties were confirmed by X-ray diffraction (XRD) (Table 1).

Series TB and TB\* display hexagonal columnar mesophases over wide temperature ranges when they bear six (TB6 and TB6\*) or nine (TB9 and TB9\*) terminal chains. TB6 and TB6\* show in their first heating cycle a peak at 162 °C and 155 °C which corresponds to a partial melting process. For all compounds the DSC curves were reproducible after the first heating and they show only one peak corresponding to the clearing point and a glass transition, which freezes the mesomorphic order at room temperature (Fig. 1). The exception to this behaviour is TB9\*, for which fluidity remains at room temperature and a glass transition was not observed upon cooling down to -20 °C (Table 1). It is remarkable that these compounds exhibit very similar transition temperatures regardless of the different number of terminal chains (TB6 vs. TB9) or whether the structure of the terminal chain is linear or branched (TB6 vs. TB6\*).

Compound **TB6** exhibits a fern-like texture by POM on cooling from the isotropic liquid and this becomes glassy at  $64 \,^{\circ}$ C, with the texture maintained but a remarkable decrease in

Compound	Phase transition $T^{a}/^{\circ}C (\Delta H/kJ \text{ mol}^{-1})$	Mesophase T <sup>b</sup> /°C	$d_{\rm meas}/{ m \AA}$	hk	$d_{\rm calc}/{ m \AA}$	Parameters <sup>e</sup>
TB3	$\operatorname{Cr} 218^{c} \mathrm{I}^{\mathrm{dec}}$	_	_	_	_	_
TB6	I 146 (0.8) Col <sub>b</sub> 64 g	g(Col <sub>h</sub> ), 20 °C	36.9	10	36.9	a = 42.6  Å
	g 74 Col <sub>h</sub> 151 (0.7) I		4.6 (br)			$S = 1572.2 \text{ Å}^2$
	_	Col <sub>h</sub> , 120 °C	37.4	10	37.4	a = 43.2  Å
	_		4.6 (br)			$S = 1615.7 \text{ Å}^2$
TB9	I 149 (2.5) Col <sub>h</sub> 58 g	g(Col <sub>h</sub> ), 20 °C	35.2	10	35.2	a = 40.3  Å
	g 71 Col <sub>h</sub> 151 (2.2) I		20.0	11	20.3	$S = 1407.3 \text{ Å}^2$
			4.6 (br)			_
	_	Col <sub>h</sub> , 130 °C	36.0	10	36.0	a = 41.6  Å
	_		4.6 (br)			$S = 1496.5 \text{ Å}^2$
TB3*	$\operatorname{Cr} 212^{c} \mathrm{I}^{\mathrm{dec}}$		—			—
TB6*	I 145 (1.2) Col <sub>b</sub> 57 g	$g(Col_{\rm h}), 20 \ ^{\circ}C^d$	33.6	10	33.6	a = 39.2  Å
	g 66 Col <sub>h</sub> 149 (1.3) I		17.2	20	16.8	$S = 1329.1 \text{ Å}^2$
			4.6 (br)			—
TB9*	I 115 (2.8) Col <sub>h</sub>	Col <sub>h</sub> , 20 °C	32.5	10	32.5	a = 37.7  Å
	Col <sub>h</sub> 120 (3.0) I		18.8	11	18.8	$S = 1229.9 \text{ Å}^2$
			12.4	21	12.3	
	_		4.6 (br)		_	_

Table 1 Phase transitions and XRD parameters for series TB and TB\*

<sup>*a*</sup> DSC data for the first cooling and second heating cycles. Onset temperatures: Cr = crystal,  $Col_h = hexagonal columnar mesophase$ , g or g(Col<sub>h</sub>) = glassy hexagonal columnar phase, I = isotropic liquid. <sup>*b*</sup> Phase and temperature of the XRD experiment. <sup>*c*</sup> DSC data for the first heating cycle, dec = decomposition. <sup>*d*</sup> Sample heated at 153 °C for 5 minutes and rapidly cooled down to room temperature. <sup>*e*</sup>  $a = (2/\sqrt{3})$  ((10) + (11) $\sqrt{3}$  + (20) $\sqrt{4}$  + (21) $\sqrt{7}$  + ...)/( $n^{\text{reflections}}$ ).



Fig. 1 DSC thermogram of compound TB6.

the optical birefringence observed for the light propagating perpendicular to the columns (Fig. 2a and b). A similar effect has been observed for compound **TB6\***, which shows a fan-shaped and spherulitic texture (Fig. 2c and d). The DSC traces only show a  $T_{\rm g}$ -like transition on cooling the mesophase. However, it is evident that the decrease in the optical birefringence is not only related to the freezing of the side chains, but indicates a more profound reorganization of the molecules. A similar phenomenon has been described for transitions from a hexagonal columnar phase to a cone-like polar columnar phase in selfassembled bent-core polycatenars due to deformation of flexible flat-disc superstructures into cones.<sup>49,50</sup>

A decrease in the optical birefringence with a change to a homeotropic texture was also observed on applying an electric field near the isotropic liquid (Fig. 2e and f). Although the polar columnar phases can be switched by applying electric fields,<sup>49,51</sup> a spontaneous polarization signal was not observed, probably due to sample instability. We were therefore unable to confirm



**Fig. 2** Microphotographs of the textures observed by POM for **TB6** (a) 140 °C, (b) 45 °C at the same area as (a); for **TB6\*** (c) 135 °C, (d) 43 °C at the same area as (c), (e) ITO planar alignment cell without applied field at 156 °C, (f) ITO planar alignment cell with applied field, 19 V  $\mu$ m<sup>-1</sup> at 156 °C at the same area as (e); and for **TB9** (g) 150 °C (h) 137 °C.

Downloaded by University of Sussex on 26 October 2012 Published on 12 March 2012 on http://pubs.rsc.org | doi:10.1039/C2JM15648B that a change from a columnar to a polar columnar phase takes place on applying a voltage, but it is interesting to note that the compound is E-field responsive, as this property has recently been described as an efficient way to prepare macroscopically oriented uniaxial materials.<sup>52</sup> By comparison, the application of an electric field under similar experimental conditions to compound **T6** induced a texture with fewer and smaller areas of homeotropic orientation than for **TB6**, indicating that ester groups in the structure of **TB6** are beneficial to the reorientation process.

Compound **TB9** shows a spherulitic texture with homeotropic domains (Fig. 2g and h). Compound **TB9\***, bearing nine chiral terminal chains, exhibits a hexagonal columnar mesophase with the lowest clearing point of the series. The mesophase of **TB9\*** remains stable at room temperature and appears with a homeotropic texture in both the heating and cooling processes.

On the other hand, compounds **TB3** and **TB3\***, bearing only three terminal chains, are crystalline solids that melt at 218  $^{\circ}$ C and 212  $^{\circ}$ C, respectively. The melting transition is not reproducible because, at such high temperatures, it is associated with a decomposition process that is also evidenced in DSC.

A direct comparison between series **TB** and series **T**, which was reported previously,<sup>45</sup> led us to conclude that TTT derivatives show a marked tendency to self-assemble into columns in spite of the different sizes of the molecule, which is elongated with alkoxyphenyl groups or alkoxybenzoyloxyphenyl groups. One difference between the two series is that compound T3, with only three decyloxy tails and shorter star branches, shows a monotropic columnar mesophase whereas compounds TB3 and TB3\* do not exhibit mesomorphism. Another difference between the two families concerns the enthalpy and transition temperature values, which are higher for series T than for series TB, indicating that the more rigid and smaller core leads to stabilization of the columnar arrangement. Nevertheless, TB compounds display higher glass transition temperatures than those in series T, a finding of particular interest for the applicability of the compounds as these vitrification processes involve freezing of the columnar order.

Azide precursors were not liquid crystalline except for A1, which bears one decyloxy terminal chain. Upon cooling the isotropic melt, droplet growth was observed by POM at 70 °C. This observation is typical of nematic mesophases but the temperature interval is very narrow and the texture quickly evolved to a myelinic texture with homeotropic areas of a smectic A mesophase (ESI<sup>†</sup>, Fig. S1). XRD studies allowed us to measure a layer spacing of 28.2 Å for the smectic A mesophase, which is in accordance with the molecular length. It seems reasonable that the rod-shape and the axial dipolar moment of molecule A1 favor mesomorphism. In contrast, the analogous compound A1<sup>\*</sup> is not liquid crystalline, which means that the presence of the shorter, branched chiral chain is sufficient to prevent mesomorphic behaviour.

#### Self-organisation in the mesophase

XRD experiments allowed us to confirm the liquid crystalline properties of the compounds (Table 1). Compounds **TB6** and **TB9**, with six and nine decyloxy tails, respectively, both gave a similar diffraction pattern at high temperatures. Each pattern

had one sharp reflection in the low-angle region and a broad diffuse halo in the high-angle region, which is characteristic of the liquid-like order of the hydrocarbon chains at 4.6 Å (Fig. 3). This pattern, together with texture observed by POM, led us to propose that the low-angle halo corresponds to the (1 0) reflection of a hexagonal columnar mesophase,53-55 giving cell parameters of 43.2 Å for TB6 and 41.6 Å for TB9. The absence of other reflections at low diffraction angles apart from the (1 0) reflection is common in diffraction patterns of hexagonal columnar mesophases<sup>41,53-56</sup> and it is due to a minimum in the form factor, which precludes the observation of peaks in this region. In the case of TB9, this situation was further confirmed by the XRD experiment at room temperature, in which two reflections in the low-angle region in a  $(1:1/\sqrt{3})$  ratio were observed. These reflections correspond to the  $(1 \ 0)$  and  $(1 \ 1)$ reflections of a hexagonal columnar organisation in the glass.

For compound **TB6\*** two reflections were observed in the small angle region in a  $(1 : 1/\sqrt{4})$  ratio and the typical halo corresponding to the liquid-like arrangement of the aliphatic chains was evident at 4.6 Å. Despite the absence of the (1 1) reflection, and also based on POM studies<sup>22,57</sup> and miscibility studies (ESI<sup>†</sup>, Fig. S3), we assume that the first reflection observed is the (1 0) reflection of a 2D-hexagonal lattice with a cell parameter of 39.2 Å. In the case of compound **TB9\***, three reflections were observed in the low-angle region in a  $(1 : 1/\sqrt{3} : 1/\sqrt{7})$  ratio and these allowed us to assign the 2D-hexagonal symmetry to the mesophase with a cell parameter of 38.3 Å. As expected, the cell parameters of the **TB** compounds are larger than the parameters obtained for **TB\*** compounds and this is a consequence of the shorter length of the 3,7-dimethyloctyloxy chains in comparison with the decyloxy tails.<sup>58</sup>

Mesophases for compounds in series **T** were previously described as hexagonal columnar.<sup>45</sup> Compounds with six and nine decyloxy tails (**T6** and **T9**, respectively) showed a regular intracolumnar distance along the columns, as revealed by the reflection corresponding to c = 3.5 Å. On considering the XRD parameters and the molecular volume, and assuming a density of



Fig. 3 XRD patterns of compounds TB6, TB9, TB6\* and TB9\*.

around 1 g cm<sup>-3</sup>, which is typical for liquid crystals, we estimated that the number of molecules per columnar stratum (Z) was two for **T6** and one for **T9**.<sup>45</sup> In the case of series **TB** and **TB**\* we did not find evidence for regular stacking along the columns (c) in the XRD experiments, but a similar estimation of the number of molecules per columnar stratum yields a value of Z = 2 for mean stacking distances of 3.7–6.2 Å (ESI<sup>†</sup>, Table S1). It is reasonable to believe that mean stacking distances should be higher than 3.5 Å in the **TB** and **TB**\* series, and increase on increasing the number of lateral chains as the measured *a* parameter decreases but the molecular volume increases and there are greater spatial requirements of the polyalkoxybenzoate terminal groups.

Taking into account the data discussed above, we can consider now a model for the packing of two molecules in each column stratum of the hexagonal columnar mesophase, which applies to compounds TB6, TB9, TB6\*, and TB9\* as well as to T3 and T6. In a columnar mesophase the molecules should be able to adopt a conformation that allows reasonably ordered stacking into columns. The possibility of considering a  $C_3$ -symmetric conformation is not plausible as we would expect a much higher cell parameter for the compounds with Z = 2 than that experimentally measured by XRD, even considering folding of the chains surrounding the core. Given that there is free rotation along the triazine-triazole bond, we propose that these molecules are in a low symmetry conformation that yields an approximately 'halfdisc shape' (Fig. 4). Bent conformations of mesogens have also been proposed for flexible star-shaped columnar liquid crystals with a benzene central core and polyester side arms.<sup>59-63</sup>



Fig. 4 Schematic drawing for the idealised arrangement of TB6 molecules to give a hexagonal columnar mesophase formed by disc-shaped dimers. This model also applies for TB9, TB6\*, TB9\*, T3 and T6.

It is interesting to note that, whereas the  $C_3$  conformation is non-polar, lowering of the symmetry by rotation along the triazine-triazole bond induces polarity that can yield an antiparallel dipolar arrangement with a neighbour occupying the same slice. This leads to a model for the hexagonal columnar mesophase with two molecules per unit cell. For example, the estimated column diameter for two molecules of TB6 in this conformation without considering any overlap is 55 Å assuming an all-trans conformation for the terminal chains.<sup>64</sup> The difference with the experimental value (a parameter) of about 10 Å could be explained by the proportion of gauche conformation in the terminal chains in order to surround the core and fill the free volume efficiently. Then, in the simplest model each TB6 molecule in the non- $C_3$  conformation would fill a half-disc that interacts with another molecule to form a disc-shaped dimer (Fig. 4), a situation consistent with the value Z = 2 and the cell parameters obtained by X-ray diffraction. This could be an oversimplified model for the TB and TB\* series because we do not observe at the XRD patterns the intracolumnar order. In fact, aggregation of antiparallel molecules could take place in such a way that the molecules are not in the same plane without the need to occupy a discrete disc, but formed by segregation of the nitrogen-rich aromatic rings and benzoate groups in the core of the columns, surrounded by the aliphatic chains at the periphery.

#### **Optical properties**

#### **Chiroptical properties**

Circular dichroism (CD) spectra were measured on thin films of the hexagonal columnar mesophase frozen at room temperature in a effort to prove the existence of supramolecular chirality for compounds **TB6\*** and **TB9\***, which contain six and nine (*S*)-3,7dimethyloctyloxy chiral tails, respectively. These chiral compounds could feasibly induce supramolecular chiral organisation in the mesophase.<sup>39,58,63,65-67</sup> Only **TB6\*** showed a rather weak signal in the absorption region of the core (275 nm, 296 nm). The band was not observed in the isotropic liquid state, which can be attributed to a barely preferential chiral organisation of the chromophores in the columnar mesophase induced by the chiral peripheral tails (Fig. 5). The spectrum recorded for **TB9\*** was CD silent, likely due to the high congestion of chiral peripheral tails that hampers a preferential helical handedness for the stacking of the cores.

#### UV-Vis absorption and photoluminescence studies

The UV-Vis absorption and emission spectra of series **TB** and **TB**\* were measured in tetrahydrofuran (THF) and cyclohexane in diluted solutions  $(10^{-6} \text{ to } 10^{-7} \text{ M})$  to ensure that the samples were molecularly dissolved. Spectra were also recorded on thin films at room temperature for systems that displayed the glassy hexagonal columnar phase in the case of the liquid crystalline compounds. The non-mesomorphic compounds **TB3** and **TB3**\* were measured as thin films prepared by drop-casting from dichloromethane solutions (Table 2).

Compounds absorb in the UV region with maxima located below 300 nm. These bands are attributed to  $\pi$ - $\pi$ \* transitions due to the high absorption coefficients. All derivatives are



Fig. 5 CD (black) and absorption spectra (blue) of TB6\* recorded in a thin film at room temperature.

luminescent in solution in the near UV-blue region of the spectrum. Series **TB** and **TB**\* show similar absorption and emission spectra, indicating that the peripheral alkoxy tails, being linear or branched, do not have any influence on the optical properties. But series **TB** and **TB**\* show emission behaviour different from series **T** due to the benzoyloxy-extended side arms (Table 3).

In series **TB** a slight blue-shift in the emission maximum is observed on increasing the number of alkoxy chains from three (**TB3**) to six (**TB6**) and nine (**TB9**) in THF solutions, but a marked red-shift occurs in cyclohexane solutions, with the emission maximum reaching the visible region of the spectrum. This means that in cyclohexane the excited state decreases in polarity and in charge transfer character on increasing the number of peripheral alkoxy chains.

The compounds in series T show an emission peak centered at 416 nm in cyclohexane solutions regardless of the number of decyloxy chains. However, a red-shift of the emission maximum is observed in THF solutions on changing from three (T3) to six (T6) and nine (T9) long tails. This finding is consistent with a strong charge transfer character and/or a conformational relaxation in the excited state, which increases in polarity on increasing the number of alkoxy chains.

Significant differences are observed in the fluorescence quantum yields, with much lower values obtained for series **TB** ( $\Phi < 0.06$ ) than for series **T** ( $\Phi = 0.18-0.43$ ).<sup>45</sup> This may be due to the free bond rotation of the benzoate group, which leads to extended non-radiative pathways competing for the relaxation of the excited state.<sup>69</sup>

In the film state all of the compounds are luminescent, with lower emission maxima for series **TB** than for series **T**, which show a blue-green luminescence in the mesophase. There is no difference in the emission maxima wavelengths between **TB6** and **TB9** and their corresponding chiral analogues **TB6\*** and **TB9\***, respectively. This is consistent with a structural organisation of the fluorophores in the columnar phase similar for both pairs of compounds, chiral and achiral. This would be in agreement with the weak CD signal observed for **TB6\*** and the CD silent spectrum recorded for **TB9\***, which indicate the weakness and absence, respectively, of a high order degree in their respective columnar organisations related to a helical disposition of the molecules.

#### Solvatofluorochromism

TTT derivatives consist of organic molecular structures in which electron-donating groups (alkoxy terminal groups) are linked through a conjugated system to an electron-accepting fragment (triazine ring). This kind of system, where intramolecular charge transfer can occur, is susceptible to showing solvatochromic properties.<sup>16,68,70-72</sup> A measurable and different solvatochromic emission effect, also called solvatofluorochromism,<sup>71</sup> was observed when the optical properties were studied in cyclohexane (apolar solvent) and THF (more polar solvent) for the series **TB** and **TB\*** (Fig. 6, left and Table 2) and series **T** (Fig. 6, right and Table 3).

For **TB** and **TB**<sup>\*</sup> the emission wavelength is lower in THF than in cyclohexane and blue-shifts were observed for **TB6** (-57 nm) and **TB9** (-83 nm) on increasing the polarity of the solvent (negative solvatochromism). In this case the ground state is more polar than the excited state. In contrast, the

Table 2 UV-Vis absorption and emission data

Compound	$\lambda_{abs}^{THF}/nm \ (\log \varepsilon)$	$\lambda_{abs}^{chex}/nm \ (\log \epsilon)$	$\lambda_{\rm em}^{\rm THF}/{\rm nm}^a$	$\lambda_{\rm em}^{\rm chex}/{\rm nm}^a$	$\lambda_{\rm em}^{\rm film}/{\rm nm}^a$	$\varPhi^b$
ТВЗ	281 (5.22)	<i>c</i>	371	c	409	
TB6	280 (4.96), 294 (4.96)	274 (4.87), 295 (4.84)	358	415	425	0.02
TB9	287 (5.23)	284 (4.91)	358	441	427	0.01
TB3*	281 (4.82)		370	c	410	
TB6*	280 (4.78), 294 (4.76)	274 (4.97), 295 (4.98)	359	416	425	0.06
TB9*	287 (5.20)	284 (4.85)	356	441	427	0.03

<sup>*a*</sup> Excitation wavelength at the absorption maximum. <sup>*b*</sup> Quantum yields in cyclohexane relative to 9,10-diphenylanthracene ( $\Phi = 0.9$  in cyclohexane solution).<sup>68 *c*</sup> Low solubility.

Table 3 UV-Vis absorption and emission data

$\lambda_{abs}^{THF}/nm^{45}$	$\lambda_{abs}^{chex}/nm$	$\lambda_{em}^{THF}/nm^{45}$	$\lambda_{\rm em}^{\rm chex}/nm$	$\lambda_{em}{}^{\rm film}\!/\!nm^{45}$
257, 289, 299 <sup>sh</sup> 264, 304	249, 284, 300 <sup>sh</sup> 262, 302	416 448 471	416 416	416 450 481
	λ <sub>abs</sub> <sup>THF</sup> /nm <sup>45</sup> 257, 289, 299 <sup>sh</sup> 264, 304 266, 301	$\begin{array}{c c} \lambda_{abs}{}^{\rm THF}/nm^{45} & \lambda_{abs}{}^{\rm chex}/nm \\ \hline \\ 257, 289, 299^{\rm sh} & 249, 284, 300^{\rm sh} \\ 264, 304 & 262, 302 \\ 266, 301 & 265, 300^{\rm sh} \end{array}$	$\begin{array}{c ccc} \lambda_{abs}{}^{\rm THF}/nm^{45} & \lambda_{abs}{}^{\rm chex}/nm & \lambda_{em}{}^{\rm THF}/nm^{45} \\ \hline 257, 289, 299^{\rm sh} & 249, 284, 300^{\rm sh} & 416 \\ 264, 304 & 262, 302 & 448 \\ 266, 301 & 265, 300^{\rm sh} & 471 \\ \hline \end{array}$	$\lambda_{abs}^{THF}/nm^{45}$ $\lambda_{abs}^{chex}/nm$ $\lambda_{em}^{THF}/nm^{45}$ $\lambda_{em}^{chex}/nm$ 257, 289, 299sh249, 284, 300sh416416264, 304262, 302448416266, 301265, 300sh471416



Fig. 6 Emission spectra for series **TB** (left) and **T** (right) in THF (solid lines) and cyclohexane (dashed lines). **TB3** in cyclohexane is not plotted due to low solubility.

opposite effect was found for series T, where a marked red-shift in emission maxima for T6 (+32 nm) and T9 (+55 nm) was observed on increasing the polarity of the solvent (positive solvatochromism). This means that the excited state is more polar than the ground state and the system will be better stabilized by polar solvents.

The emission spectra of thin films at room temperature (in the glassy hexagonal columnar phase for the liquid crystalline compounds) for series TB are more similar to the spectra in cyclohexane solution than those in THF, whereas for series T the emission spectra in thin films match those in THF solutions. Solvatochromic properties enable information to be gained about the polarity of the media. This method has been used to successfully characterise not only solvents but also systems such as solid surfaces, stationary phases for chromatography, or supramolecular media such as cyclodextrins and micelles.<sup>70</sup> The fact that the mesogenic compounds of series T and TB show solvatofluorochromic properties means that they can act as probes to characterise the polarity of the columnar hexagonal mesophases. Comparison of the spectra obtained from solutions and films allows us to estimate the polarity of the environment of the fluorophores, i.e., of the intrinsic liquid crystal. This allows us to conclude that in the mesophase the polarity of the excited state is low and similar to the apolar cyclohexane in TB6 and TB9, and more polar and similar to THF in T6 and T9. In other words, the TB molecules have a more polar ground state than T molecules in the mesophase, and their dipole moment decreases in the excited state.

One limitation of solvatofluorochromism is that it only gives an indication of the overall polarity of the probe environment. As a result, although we can infer that **TB** molecules are more dipolar than **T** molecules in the condensed phase and that the overall polarity of the liquid crystal phases that consist of **TB** as a macroscopic medium is higher than for series **T**, a direct comparison with the symmetry and conformation of the molecules in the mesophase cannot be made. However, the results are consistent with the fact that **TB6** films can be oriented under electric fields more easily than **T6**.

#### **Redox properties**

Cyclic voltammetry (CV) studies of compounds **TB/TB**\* were performed in oxygen free dichloromethane solutions. The electrochemical data are summarised in Table 4. Compounds did not show any oxidation process on scanning from 0 to +2.2 V. All compounds showed a reversible reduction wave at around -1.65 V, relative to the Ag/AgCl reference electrode, irrespective of the number of alkoxy chains. For comparative purposes and LUMO calculations the values have been also referenced to the ferrocene/ferrocenium couple (FOC), and were about -2.13 V. This corresponds to LUMO energy levels of around -2.67 eV.

Series **TB** has similar electron-acceptor properties with respect to other triazine derivatives such as 2,4,6-triphenyl-1,3,5-triazine, which has a reduction potential of -2.09 V *versus* FOC and a LUMO energy of -2.71 eV.<sup>73</sup> In comparison with the previously reported series **T**,<sup>45</sup> for which a first reduction potential of

Table 4	Electrochemical	behaviour
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Compound	$\begin{array}{c} (E_{1/2}^{\mathrm{red}} vs.\\ \mathrm{Ag/AgCl})/\mathrm{V} \end{array}$	$(E_{1/2}^{red} vs. FOC^{a}/V$	$E_{g}^{b}/eV$	LUMO <sup>c</sup> /eV
TB3	-1.65	-2.13	3.89	-2.67
TB6	-1.65	-2.13	3.86	-2.67
TB9	-1.65	-2.13	3.86	-2.67
TB3*	-1.63	-2.11	3.87	-2.69
TB6*	-1.64	-2.12	3.84	-2.68
TB9*	-1.65	-2.13	3.84	-2.67

<sup>*a*</sup>  $E_{1/2} = 0.48$  V vs. Ag/AgCl. <sup>*b*</sup> Optical bandgap calculated from THF solution absorption edges. <sup>*c*</sup> Calculated as the difference between -4.8 eV and  $E_{1/2}^{red}$  vs. FOC.

-1.28 eV or -1.33 eV *versus* FOC and LUMO values of -3.47 V or -3.52 V was found, series **TB** showed more negative reduction potentials, higher LUMOs and higher optical bandgaps.

Electrochemistry shows that the reduction wave is independent of the number of alkoxy tails. The fact that we observe the same voltammogram is due to that adding alkoxy peripheral chains at the *meta* position of the external aromatic ring does not affect significantly the reduction process. The redox processes are ground-state properties, and are related to the absorption spectra, which in fact is almost the same for all compounds. The emission properties, that is, the ones not related to the ground state but to the excited state, are the ones that are changed with the number of peripheral chains, indicating that the redox properties of the excited state would be also different.

As the absorption characteristics are quite similar in both series **T** and **TB**, the increase in the bandgap in the latter is mainly caused by a shift of the LUMO value to higher energy rather than a decrease of the HOMO value, although the less-strongly donating benzoyloxy group should also decrease the HOMO energy to some extent.<sup>74</sup> Finally, the results shown in Table 4 indicate that the introduction of the benzoyloxy moiety into the molecular structure (series **TB**) leads to a system that is more difficult to reduce, *i.e.*, with poorer electron-accepting properties than in series **T**.

## Conclusions

The synthesis of new derivatives based on the TTT core, 2,4,6tris(1',2',3'-triazol-4'-yl)-1,3,5-triazine, has been achieved by the one-pot reaction which combines a triply deprotection and CuAAC "click chemistry" procedure. For this purpose novel aromatic azides were prepared with polyalkoxybenzoyl groups and liquid crystalline behaviour was found in one example.

The TTT-derived star-shaped compounds showed excellent liquid crystalline properties, with hexagonal columnar mesomorphism observed over wide temperature ranges. The hexagonal order was frozen in a glassy state upon cooling, with the selforganisation of the columnar arrangement preserved at room temperature. A model for the arrangement of the molecules in the mesophase is proposed, based on the XRD data, in which two molecules with non- $C_3$  symmetry but a "half-disc" conformation are arranged in a columnar stratum. Furthermore, the mesophases show luminescence in the blue-green region of the visible spectrum depending on the peripheral substitution and molecular structure. In solution, the luminescence is moderate for series T ( $\Phi = 0.18-0.43$  in cyclohexane) but is decreased by the inclusion of a benzoyloxy unit in the arms in the series **TB/TB\*** ( $\phi < 0.06$  in cyclohexane). Positive and negative solvatofluorochromism is observed for series T and TB/TB\*, respectively, indicating that the polarities of the ground and excited states of the compounds are drastically affected by the introduction of the benzoyloxy moiety in the star arms and the grafting of long alkyloxy chains. The solvatofluorochromic properties of the molecules allowed us to characterise the polarity of the hexagonal columnar mesophase, which is different depending on the series. The electrochemical characterisation of compounds TB/TB\* reveals a weaker electron-accepting character with respect to series T.

Finally, as a proof of principle, the CuAAC 'click chemistry'<sup>75</sup> procedure designed for the 1,3,5-triazine core proved to be a versatile way to decorate the periphery of this acceptor core with triazole functional spacers<sup>76</sup> and aromatic donors. This approach is useful to obtain octupolar columnar liquid crystals with interesting optical and electronic properties.

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