Liquid Crystals

Supramolecular Columnar Liquid Crystals Formed by Hydrogen Bonding between a Clicked Star-Shaped *s*-Triazine and Benzoic Acids

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Abstract: A star-shaped tris(triazolyl)triazine is shown to establish hydrogen-bond interactions with polycatenar benzoic acids. The formation of hydrogen-bonded triazine/acid complexes has been demonstrated both in solution and in bulk by different techniques. The complexes, mainly formed by nonmesogenic components, all show enantiotropic hexagonal columnar mesomorphism, which relies on the formation

Introduction

Since the earliest reported examples,^[1] supramolecular liquid crystals, and, in particular, those showing columnar arrangements, have been considered to be useful for the development of strategies that increase both structural complexity and molecular order in functional materials.^[2] These systems can form the same liquid-crystal phases seen in covalent liquid crystals but, generally, they are much easier to prepare because the smaller building blocks self-assemble spontaneously to give the columnar arrangements. In addition, these systems are dynamic, which allows a rapid response to external stimuli.

One approach to obtain supramolecular columnar liquid crystals is by hydrogen-bonding of a heterocyclic core that does not show the columnar phase with complementary peripheral units, such as some readily accessible promesogenic carboxylic acids.^[3] There are only a few examples of systems that have been produced by following this method,^[4] although it is an interesting and useful strategy to access novel functional columnar nanostructures when a π -conjugated core is used.^[5] Therefore, to obtain novel supramolecular columnar liquid crystals by interaction with carboxylic acids, novel discot-

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of hydrogen-bond complexes in a triazine/acid ratio of 1:3. This approach combines the straightforward synthesis of a nonmesomorphic triazine core by click chemistry, and the preparation of a supramolecular complex, providing a much more convenient route than covalent synthesis to modify the periphery of triazine discotics and thus to modulate their functionality.

ic building blocks that are able to interact through hydrogen bonding are necessary. In this context, we studied the hydrogen-bonding ability of a novel π -functional core bearing triazine and triazole rings. The results of our investigation are reported herein.

The 1,3,5-triazine ring (s-triazine) is a star-shaped π -functional unit^[6] that has been used to obtain columnar liquid crystals.^[7] In addition, triazine-based cores, such as triarylaminotriazine^[8] or *N*-alkylmelamine derivatives,^[9] can also form hydrogen bonds with carboxylic acids, providing columnar mesomorphic behavior. Additionally, the 1,2,3-triazole ring, which is easily accessible through click chemistry,^[10] is very attractive for functional materials,^[11] and also for considering supramolecular interactions.^[12] The formation of hydrogen bonds between 1,2,3triazole and anions is well-known,^[13] but this ring can also form hydrogen bonds with carboxylic acids.^[4d,e, 14] For example, hydrogen-bonded complexes consisting of a C₃-symmetric tris(triazolyl)benzene unit with benzoic acids in a 1:3 stoichiometry, has been shown to exhibit columnar mesomorphism.^[4d] Moreover, click chemistry allows the appropriate modification of the periphery of the molecules to obtain discotic liquid crystals.^[15] Indeed, the versatile 1,3,5-triazine scaffold can be triply functionalized with triazole rings by click chemistry to give the star-shaped 2,4,6-tris(triazolyl)-1,3,5triazine.^[16] This core can be readily prepared and gives rise to derivatives with columnar mesomorphism.^[16,17]

In the present work, we go a step further and explore the ability of the core described above to form hydrogen bonds because of the presence of triazine and triazole rings. In particular, we study the formation of supramolecular hydrogenbonded complexes between a tris(triazolyl)triazine derivative and several benzoic acids to obtain columnar liquid crystals that could be, in this way, easily modulated in their periphery.

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The tris(triazolyl)triazine derivative used as a core (T3C₄) had a *p*-butoxyphenyl substituent in each triazole ring (Scheme 1) and was not liquid crystalline. The butoxy terminal chains aid solubility in organic solvents, which is important for the formation of the supramolecular complexes by dissolution of a mixture of the components.



Scheme 1. Synthetic procedure for the preparation of the tris(triazolyl)-triazine derivative T3C₄.

To study the formation of the supramolecular complexes and the induction of columnar mesomorphism, three 3,4,5-trisubstituted benzoic acids were used. Two of these bear three alkoxy chains of ten carbon atoms (A1) or twelve carbon atoms (A2), which allows the influence of the length of the alkoxy chains on the stability of the complex to be compared. The third acid is a benzoic acid with three alkoxy terminal chains of twelve carbon atoms in a dendron-like aromatic core (A3). By using the T3C₄ core and these carboxylic acids, mixtures of 1:3 stoichiometry were prepared. The structures of the target supramolecular complexes are shown in Figure 1. In addition to the hydrogen bond between the hydroxyl group of the benzoic acids and the nitrogen atoms in the triazine and triazole rings, we observed the formation of another hydrogen bond between the carbonyl group of the acid and the hydrogen atom situated at the C4 position of the 1,2,3-triazole ring, which is allowed by the electropositive character of this triazole hydrogen.^[4d]



Figure 1. Molecular structure of the target supramolecular complexes.

Results and Discussion

Synthesis

The 2,4,6-tris[1'-(4"-butoxyphenyl)-1',2',3'-triazol-4'-yl]-1,3,5triazine core (T3C₄) was synthesized by a copper-catalyzed alkyne-azide cycloaddition (CuAAC) "click reaction". Given that the required alkyne 2,4,6-tris(ethynyl)-1,3,5-triazine is unstable, a previously described one-pot procedure,^[16] which uses the protected precursor 2,4,6-tris[(trimethylsilyl)ethynyl]-1,3,5-triazine,^[18] was used. In this one-pot reaction, the alkyne groups of 2,4,6-tris[(trimethylsilyl)ethynyl]-1,3,5-triazine were deprotected and allowed to react in situ with the aromatic azide in the presence of catalytic copper(I) at room temperature (Scheme 1). The reaction gave the desired product in a moderate yield (33%). The required aromatic azide, 1-azido-4-butoxybenzene, was synthesized by diazotization of 4-aminophenol followed by reaction with sodium azide^[16] (Scheme 1). The acids A1–A3 were synthesized by using known procedures.^[8c]

The hydrogen-bonded complexes were prepared by dissolving a mixture of the tris(triazolyl)triazine core and the corresponding benzoic acid derivative in a 1:3 proportion, respectively, in dichloromethane. After evaporation of the solvent by continuous stirring at room temperature, the obtained mixtures were subjected to a thermal treatment consisting of heating to the isotropic liquid and then cooling to room temperature. The thermally treated mixtures were observed by polarizing optical microscopy (POM), and they appeared as homogeneous materials with liquid crystalline behavior, which suggested that the complexes had been formed.

Formation of hydrogen-bonded complexes in solution

To study the interaction between the $T3C_4$ and the different benzoic acids in solution when mixed in a 1:3 ratio, ¹H NMR experiments in $[D_2]$ dichloromethane were performed. Assuming

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that there is fast exchange between the complex and its components in solution, strong evidence of hydrogen-bonding interactions between the $T3C_4$ core and acid molecules was found in the solution ¹H and ¹³C NMR spectra of the complexes.

The ¹H NMR spectra of the $T3C_4$ core, the acid A1, and a mixture of both components in a 1:3 ratio are compiled in Figure 2. It can be observed that the signal corresponding to



Figure 2. ¹H NMR spectra of the core $T3C_4$ (0.1 M), the acid **A1** (0.3 M), and their mixture in [D₂]dichloromethane, maintaining these concentrations.

the hydrogen of triazole (H_c) undergoes a shift from δ = 8.90 ppm in pure T3C₄ to δ = 8.98 ppm when the core and the acid are mixed, which indicates that this proton interacts through hydrogen bonding with the carbonyl group of the acid. Simultaneously, the aromatic protons of T3C₄ (H_e and H_f) show significant shielding. This upfield shift suggests aggregation of the complex due to π -stacking.

To check the possibility of self-aggregation of the core by π -stacking, ¹H NMR spectra of pure T3C₄ at different concentrations were recorded (Figure 3). On increasing the concentration, all the signals, including the triazole proton H_c, are clearly shifted upfield, which is consistent with π -stacking aggregation.

By comparing Figure 2 and Figure 3 at the same concentration of T3C₄ core (0.1 M), it can be seen that the presence of the acid in a 1:3 ratio causes further upfield shift of the aromatic protons H_e and H_f, which can indicate that aggregation by π -stacking is even more favored upon formation of a hydrogen-bonded complex. Interestingly, the triazole proton H_c does not show an upfield shift but displays a downfield shift for the complex, which confirms that this proton is involved in a hydrogen-bonding interaction.





Figure 3. ¹H NMR spectra of the core T3C₄ in $[D_2]$ dichloromethane at different concentrations (0.1, 0.025, and 0.002 M).

The ¹H NMR spectra of the mixture T3C₄ and **A1** in a 1:3 ratio at different concentrations in [D₂]dichloromethane were also recorded (Figure 4). On increasing the concentration, all the signals corresponding to T3C₄ shifted upfield, which is consistent with π -stacking aggregation of the complex, as observed for the core itself.



Figure 4. ¹H NMR spectra of the mixture T3C₄ and **A1** in a 1:3 ratio in $[D_2]$ dichloromethane at different concentrations (0.1 and 0.002 M, referred to T3C₄).

Similar results to those discussed above, were observed for mixtures of the core $T3C_4$ and acids A2 (Figures S7, S8) or A3 (Figures S12, S13), the spectra for which are included in the Supporting Information.

To determine the stoichiometry of the complexes in solution, Job's plot analysis was applied to ¹H NMR experiments in [D₂]dichloromethane solutions. The Job's plot for the hydrogen of the triazole group shows a maximum at $\chi_A = 0.5$, which indicates that core–acid association occurs in a 1:1 stoichiometry in [D₂]dichloromethane solution (see the Supporting Information, Figure S14). This result is similar to those obtained for previously reported complexes between melamines and carboxylic acids, and does not preclude the formation of 1:3 complexes in the mesophase.^[9]

Thermal properties and mesomorphic behavior

The thermal properties of the hydrogen-bonded complexes and their individual components were studied by using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC).

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The tris(triazolyl)triazine T3C₄ is not a liquid crystal. It was obtained as a crystalline solid that melted at 173 °C and then, on cooling, an amorphous solid with a glass transition about 60 °C was obtained. Acids **A1** and **A2** (with three alkoxylic chains, $-OC_{10}H_{21}$ and $-OC_{12}H_{25}$, respectively) do not display mesomorphic properties.^[19] However, acid **A3** exhibits hexagonal columnar mesomorphism (Cr 65 Col_h 144 I), in which the stacking units consist of H-bonded dimers.^[8c, 20]

As mentioned above, all the complexes were obtained as homogeneous materials with mesomorphic behavior within broad temperature intervals. Furthermore, mesomorphic properties were observed from nonmesogenic components in the case of $T3C_4$ -A1 and $T3C_4$ -A2, which also provides evidence for the formation of the hydrogen-bonded complexes. Characteristic textures of columnar mesophases were observed by POM for all the complexes (Figure 5). The thermal properties (transition temperatures and enthalpies) of the hydrogen-bonded complexes are given in Table 1.

The complex $T3C_4$ -**A3** can retain the mesophase at room temperature, as deduced from the DSC cooling scan (see the Supporting Information, Figure S17). However, for $T3C_4$ -**A1** and $T3C_4$ -A2, the DSC thermograms are not fully clear. For these complexes, partial crystallization or partial separation of the components can be deduced from the corresponding DSC cooling scans. Nevertheless, the observations with POM clearly show that phase separation does not occur, and homogeneous materials that uniformly melt to the isotropic liquid are obtained. The mesophases of complexes $T3C_4$ -**A1** and $T3C_4$ -**A2** are metastable at room temperature and they crystallize on heating, as deduced from the appearance of cold crystalliza-



Figure 5. Microphotographs of the textures observed by POM for a) T3C₄-A1, Col_h, 50 °C (cooling); b) T3C₄-A2, Col_h, 45 °C (cooling); and c) T3C₄-A3, Col_h, 122 °C (cooling).

Table 1. Thermal properties of the hydrogen-bonded complexes and structural parameters measured by X-ray diffraction of the respective col- umnar mesophases.						
Complex	Thermal properties (\mathcal{T} [°C], (ΔH [kJ mol $^{-1}$])) ^[a]	Lattice para- meters [Å]				
T3C ₄ - A1	l 71 (2.8) Col _h 9 (0.7) ^[b] Col _h + Cr Col _h + Cr 30 (–1.4) Cr 37 (5.6) Col _h 85 (2.1) l	a=33.5				
T3C₄- A2	I 67 (2.5) Col _h 20 (19.1) ^[b] Col _h + Cr Col _h + Cr 30 (-19.3) Cr 55 (47.9) Col _h 82 (1.5) I	a=35.6				
T3C ₄ - A3	l 136 (12.1) Col _h Col _h 142 (12.4) l	a=42.3 c=3.4				
[a] DSC data of the first cooling process and the second heating process at a rate of 10° Cmin ⁻¹ . Temperatures at the maxima of the peaks are						

at a rate of 10°C min⁻¹. Temperatures at the maxima of the peaks are given. I: isotropic liquid; Col_h : hexagonal columnar phase; Cr: crystalline phase; [b] partial crystallization.

tion processes in the corresponding DSC heating scans (see the Supporting Information, Figures S15 and S16).

The textures observed by POM are characteristic of hexagonal columnar mesophases, although the assignment of the type of mesophase and the determination of the lattice parameters were achieved by X-ray diffraction studies (Table 1). X-ray experiments were carried out on samples that were cooled from the isotropic liquid. For complexT3C₄-**A3**, which can retain the mesophase, the experiments were performed at room temperature (Figure 6). For complexes T3C₄-**A1** and T3C₄-**A2**, the mesophases of which are metastable at room temperature, the experiments were carried out at higher temperatures (see the Supporting Information, Figures S18 and S19), where the mesophases are known to be stable according to the DSC thermograms.



Figure 6. X-ray diffraction patterns of T3C₄-A3: a) Room temperature; b) room temperature, partially aligned sample. The reinforced reflections (arrows) and the rubbing direction (dashed line) are indicated.

The X-ray patterns of all the three complexes contain a single diffraction maximum at small angles. In the absence of other reflections, it is difficult to unambiguously assign the type of mesophase on the basis of X-ray diffraction data alone. Nevertheless, similar behavior has been found in other structures that were previously described as hexagonal columnar phases, and it is due to a minimum in the form factor, which precludes the observation of peaks in this small-angle region.^[8c, 16, 21] The observation of only one diffraction maximum could also be consistent with lamellar phases, as described for polycatenar disc-like ionic complexes with peripheral long tails.^[22] Unlike these ionic complexes, the peripheral long tails in the present complexes are contained in benzoic acid derivatives. These acids bring additional aromatic rings radiating from the tris(triazolyl)triazine core that contribute to the planar disk-like core, making it prone to $\pi\mbox{-stacking}.$ Given the complex structure and considering the textures observed by POM, we suggest that these complexes show hexagonal columnar mesomorphism, Col_h. All the complexes show a diffuse halo at 4.5 Å in the wide-angle region due to the liquid-like order between the disordered aliphatic chains. Additionally, an outer diffuse halo at 3.4 Å is observed for complex T3C₄-A3, which is indicative of a periodic stacking distance along the columns (parameter *c*). The value of the parameter *c* for this complex is consistent with the stacking distance found in columnar mesophases of tris(triazolyl)triazines.^[16] Moreover, in a partially oriented diagram, which was measured for a mechanically treated sample of T3C₄-A3 (Figure 6b), this latter reflection is reinforced along the alignment direction, whereas the low-angle reflection is reinforced in the perpendicular direction. This pat-

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tern is consistent with a columnar mesophase in which columns are oriented along the rubbing direction.

Assuming that the low-angle maxima correspond to the (100) reflection of the corresponding hexagonal columnar mesophases, the lattice parameters (*a*) of the complexes were determined from these maxima. As can be expected, the hexagonal lattice constant *a* increases as the length of the aliphatic chain of the benzoic acid derivative is increased. Thus, for complex T3C₄-A2, with twelve carbon atoms in each chain, the hexagonal parameter *a*=35.6 Å is larger than the value for complex T3C₄-A1 (*a*=33.5 Å), with decyloxy chains. Furthermore, the hexagonal lattice constant measured for complex T3C₄-A3 is significantly larger (*a*=42.3 Å) because of the extended size of acid A3.

In addition, the density of the complexes was calculated on the basis of the parameters measured by X-ray diffraction. The relationship between the density (ρ) of the complexes in the mesophase and the measured lattice parameters is given by the equation $\rho = (M \cdot Z)/(N_A \cdot V)$, where *M* is the molar mass of the 1:3 complex, *Z* is the number of molecules in the unit cell, N_A is Avogadro's number, and *V* is the unit cell volume ($V=a \times a \sqrt{3}/2 \times c \times 10^{-24}$). The density of the complexes (on the assumption that Z=1) was calculated to be close to 1 g cm⁻³, which is reasonable for organic compounds, and thus is in agreement with the formation of discotic 1:3 complexes with one complex per stacking unit.

Formation of the complexes in the mesophase

Further confirmation of the formation of 1:3 complexes in the mesophase was attained from studies performed in the mesophase, which were based on infrared spectroscopy (IR), solid-state NMR and fluorescence spectroscopies.

As described for the X-ray experiments, the IR spectra of the complexes were recorded at temperatures at which the mesophases are known to be stable on cooling from the isotropic states: for complex $T3C_4$ -A3, the experiment was carried out at room temperature, and for complexes $T3C_4$ -A1 and $T3C_4$ -A2, the spectra were recorded at 60°C (see the Supporting Information, Figures S21 and S22).

As a representative example that demonstrates the formation of the hydrogen-bonding associations, the infrared spectra of $T3C_4$, A3, and the corresponding 1:3 complex $T3C_4$ -A3 are very revealing (Figure 7). A significant difference between the C=O stretching bands in the acid and in the complex spectra can be observed. In the acid spectrum, two C=O stretching bands appear at 1667 and 1733 cm⁻¹, which correspond to the dimeric form and the free form of A3, respectively. In the IR spectrum of complex $T3C_4$ -A3, however, a single band is observed at an intermediate position, at 1709 cm⁻¹. Moreover, significant changes in the band corresponding to the hydroxyl group can be observed when the complex is formed. In the acid spectrum, two O-H stretching bands appear: the typical broad band between 3600 and 2400 cm⁻¹, due to the dimeric form of the acid, and an additional band between about 3550 and 3150 cm⁻¹, which corresponds to the free form. In the spectrum of complex T3C4-A3, this latter band does not





Figure 7. IR spectra of T3C₄, A3, and complex T3C₄-A3 (room temperature) recorded on KBr pellets. On the right, an expansion of the 1850–1400 cm⁻¹ region is shown.

appear, and only the broad band related to hydrogen-bonding interactions is observed. Additionally, bands that correspond to the heterocyclic rings shift to slightly higher wavenumber (e.g., from 1566 to 1571 cm⁻¹) when the complex is formed.

The ¹³C cross-polarization magic-angle spinning (¹³C CPMAS) NMR spectrum could be recorded at room temperature in the Col_h mesophase for complex T3C₄-A3, providing strong evidence for the formation of the complex according to a 1:3 stoichiometry. Figure 8 shows the spectrum of this complex compared with those of its corresponding components, acid A3 and core T3C₄.

The spectrum of acid A3 shows two signals corresponding to the carbon atom of the carbonyl group, at 172.2 ppm and 166.0 ppm, which correspond to the dimeric form and the free form of A3, respectively. These signals are not visible in the ¹³C NMR spectrum of the complex but, instead, a new signal appears overlapped with the carbon atom of the triazine ring. This signal can be interpreted as corresponding to the carbon atom of the carbonyl group forming hydrogen-bonding interactions with the core. Other signals of both the core and the acid are also shifted when the complex is formed in the bulk, and this can be related to differences in the stacking order of the complex with respect to the core or the acid, separately. In general, the signals corresponding to the core are shifted upfield upon complexation. Triazole carbon atoms b and c, aromatic carbon atoms e and f, and the carbon atoms linked to the oxygen atom in the terminal chains, \mathbf{h} , are shifted upfield upon complexation. With respect to the acids, some of their aromatic signals shift slightly to lower fields upon formation of the complex. Finally, the signals of the aliphatic chains of both the acid and the core undergo significant changes upon complexation, likely due to conformational changes.

A comparative study of the photoluminescence of both the complexes and their corresponding pure components also revealed differences in their emission behavior (Table 2). The fluorescence spectra were recorded on films, which were prepared by cooling the compounds from their isotropic liquid state between quartz plates. The spectra of the individual components, core and acids, were recorded at room temperature in their solid phases obtained by cooling the isotropic liquid. As was performed for X-ray and IR experiments, the fluores-





Figure 8. ¹³C CPMAS NMR spectra of $T3C_4$, **A3**, and their corresponding 1:3 complex, $T3C_4$ -**A3**. The most representative signals that shift upon complexation are indicated. All the spectra were recorded at room temperature.

Table 2. Fluorescent data (excitation and emission wavelengths) of thin films.					
Compound	λ_{exc} [nm]	λ_{em} [nm]			
A1	275	344			
A2	275	344			
A3	280	380			
T3C ₄	286	423			
T3C₄- A1	290	405			
T3C₄- A2	290	405			
T3C ₄ - A3	290	405			

cence and excitation spectra of the complexes were recorded at temperatures at which the mesophases are known to be stable: for complex $T3C_4$ -**A3** the experiments were carried out in the columnar mesophase at room temperature (Figure 9 and S27), and for complexes $T3C_4$ -**A1** and $T3C_4$ -**A2** the spectra were recorded at 60 °C (see the Supporting Information, Figures S23–S26). The absorption spectrum of complex $T3C_4$ -**A3** could be measured in the mesophase at room temperature and was similar to its excitation spectrum (see the Supporting Information, Figure S28).

The core $T3C_4$ shows an emission band in the blue region of the visible spectrum (423 nm), whereas the acids show emis-



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Figure 9. Emission spectra of $T3C_4$, A3, and complex $T3C_4$ -A3 in thin films at room temperature.

sion at lower wavelengths, in the UV region (344 or 380 nm). In contrast, the fluorescence spectra of the complexes show a band at 405 nm. The disappearance of the emission band of the acid and the observed redshift support the conclusion that hydrogen-bonded complexes are formed.^[4d] This is interesting in terms of having an additional technique to monitor the formation and stability of these supramolecular complexes by simply recording the emission spectra of the film.

Conclusion

New supramolecular complexes based on hydrogen-bonding interactions between a tris(triazolyl)triazine derivative (T3C₄) and three molecules of polycatenar benzoic acids (A1, A2, A3) have been prepared. When these components are mixed in [D₂]dichloromethane in a 1:3 ratio, respectively, NMR experiments have demonstrated the interaction between the hydrogen of the triazole ring of the tris(triazolyl)triazine core and the carboxylic acids. This interaction leads to the formation of a hydrogen-bonded complex, with the 1:1 stoichiometry of the species being stable in solution, which additionally show significant tendency to self-aggregate by π -stacking.

In the bulk, all three complexes, mainly formed by nonmesogenic components, show hexagonal columnar mesomorphism at different ranges of temperatures, as demonstrated by POM, DSC, and X-ray diffraction experiments. This behavior is consistent with the formation of T3C₄-A1, T3C₄-A2, T3C₄-A3 complexes with a 1:3 stoichiometry. Further evidence for the formation of the 1:3 complexes has been obtained from the study of the mesomorphic materials by different techniques such as infrared spectra, solid-state NMR (¹³C CPMAS) and fluorescence spectroscopy. These results suggest a decisive role of mesogenic driving forces (mainly π -stacking) to help the formation of the 1:3 complex in the bulk.

Finally, the preparation and study of these complexes provides a versatile approach to ordered materials that can be readily prepared and easily modified in their periphery, to modulate their functionality.



Experimental Section

General remarks

All reagents were purchased from Aldrich and used without further purification. Anhydrous dichloromethane and THF were purchased from Scharlab and dried by using a solvent purification system. ¹H and ¹³C NMR spectra were acquired with a Bruker AV400 spectrometer. The experiments were performed at RT in deuterated solvents (CDCl₃ or [D₂]dichloromethane). Chemical shifts are given in ppm relative to TMS and the solvent residual peak was used as the internal standard. Solid-state NMR experiments were performed by using a double resonance (1H-X) probe with a rotor of 2.5 mm diameter, and the spinning frequency was set to 15 kHz. Data were acquired at 298 K and chemical shifts are referenced to TMS. The 1 H and 13 C pulse length were 8 and 5.7 μ s, respectively, and the CP contact time was 1.5 ms. The recycle delay was 5 s. The pulse sequence employed consisted of ramped cross-polarization with spinal-64 decoupling. IR spectra were recorded with a Bruker Vertex 70 FTIR spectrometer. The samples were prepared on KBr pellets with a concentration of the product of 1-2% (w/w). A temperature controller was adapted to measure the spectra at different temperatures. Mass spectra were obtained with a MICROFLEX Bruker (MALDI+) spectrometer with a dithranol matrix. Elemental analyses were performed with a PerkinElmer 240C microanalyzer. The mesophases were examined by polarizing optical microscopy with a polarizing optical microscope Olympus BX51 equipped with an Olympus DP12 digital camera and connected to a Linkam THMS600 hot-stage and a Linkam TMS94 controller. Transition temperatures and enthalpies were obtained by differential scanning calorimetry with DSC TA instruments Q-20 and Q-2000 at heating and cooling rates of 10°C min⁻¹. The apparatus were previously calibrated with indium (156.6 $^{\circ}$ C, 28.44 Jg⁻¹). Powder X-ray experiments were performed with a pinhole diffractometer (Anton Paar) operating with a point focused Ni-filtered Cu-K α beam. The samples were held in Lindemann glass capillaries (0.7 and 0.9 mm diameter) and heated with a variable-temperature attachment. The diffraction patterns were collected on photographic films. Fluorescence spectra were recorded with a PerkinElmer LS50B spectrophotometer. Films were prepared between two quartz plates by heating the compounds to their isotropic liquid and cooling to the experiment temperatures and they were measured by front-detection.

Synthesis and characterization of T3C₄

1-Azido-4-butoxybenzene (1): 4-Butoxyaniline (2.50 g, 15.1 mmol) was dissolved in an aqueous mixture consisting of H₂O (40 mL), glacial acetic acid (90 mL), and HCl conc. (8 mL). NaNO₂ (1.22 g, 17.7 mmol) dissolved in H₂O (10 mL) was added slowly to the mixture at 0°C. The mixture was stirred for 5 min and then NaN₃ (1.10 g, 16.9 mmol) dissolved in H_2O (10 mL) was slowly added. The reaction was stirred at 0°C for 90 min and the mixture was then extracted with CH₂Cl₂. The organic layers were combined and washed with an aqueous solution of NaOH (10%). The organic layer was dried over MgSO4 and the solvent was evaporated. The crude oil was dried at 50 °C under vacuum for 4 h and the product was purified by column chromatography with silica gel stationary phase and hexane as eluent to give the product as an orange oil. Yield: 93% (2.71 g); ¹H NMR (400 MHz, CDCl₃): $\delta = 6.97-6.92$ (m, 2H; ArH), 6.91-6.86 (m, 2H; ArH), 3.94 (t, J=6.5 Hz, 2H; OCH₂), 1.83–1.70 (m, 2H; CH₂), 1.55–1.43 (m, 2H; CH₂), 0.98 ppm (t, J =7.4 Hz, 3 H; CH₃); ¹³C NMR (100 MHz, CDCI₃): δ = 156.7, 132.2, 120.1,

115.9, 68.2, 31.4, 19.4, 14.0 ppm; IR (NaCl): $\tilde{\nu} = 2959$ (Csp³–H), 2109 (N₃), 1504 (Ar), 1245 cm⁻¹ (C–O).

2,4,6-Tris[1'-(4''-butoxyphenyl)-1',2',3'-triazol-4'-yl]-1,3,5-triazine 2,4,6-Tris[(trimethylsilyl)ethynyl]-1,3,5-triazine^[18] (T3C₄): (1.00 a, 2.7 mmol), 1 (1.61 g, 8.4 mmol), sodium ascorbate (0.16 g, 0.8 mmol), and $CuSO_4 \cdot 5 H_2O$ (0.10 g, 0.4 mmol) were dissolved in a mixture of THF/H₂O (1:1, 35 mL) under an argon atmosphere. The mixture was stirred at RT for 3 min and then tetrabutylammonium fluoride (TBAF; 1 m in THF, 8.4 mL, 8.4 mmol) was added. The reaction was stirred at RT in the dark for 16 h. Water (20 mL) was then added and the mixture was extracted with CH_2CI_2 (3×60 mL). The combined organic layers were dried over MgSO₄ and the solvent was evaporated. The residue was purified by column chromatography on silica gel, gradually increasing the polarity of the eluent from CH₂Cl₂ to CH₂Cl₂/ethyl acetate 9.5:1 and further recrystallization from ethanol, giving the product as a yellowish solid. Yield: 33% (0.66 g); ¹H NMR (400 MHz, [D₂]dichloromethane): $\delta = 9.03$ (s, 3H; H triazole), 7.86-7.76 (m, 6H; ArH), 7.17-7.05 (m, 6H; ArH), 4.06 (t, J = 6.5 Hz, 6H; OCH₂), 1.86–1.77 (m, 6H; CH₂), 1.59–1.48 (m, 6H; CH₂), 1.01 ppm (t, J=7.4 Hz, 9H; CH₃); ¹³C NMR (100 MHz, $[D_2]$ dichloromethane): $\delta = 167.3$, 160.5, 146.4, 130.3, 126.2, 122.7, 115.9, 68.8, 31.8, 19.8, 14.2 ppm; IR (KBr): $\tilde{\nu} = 2958$ (Csp³–H), 2932 (Csp³-H), 2872 (Csp³-H), 1611, 1566, 1513 (arC-C, triazole), 1249 (C–O), 1169 cm⁻¹ (C–O); MS (MALDI+, dithranol): *m/z*: 749.4 $[M+Na]^+$, 1476.1 $[M_2+Na]^+$; elemental analysis calcd (%) for C₃₉H₄₂N₁₂O₃·H₂O: C 62.89, H 5.95, N 22.57; found: C 62.76, H 5.99, N 22.23.

Synthesis and characterization of A1, A2, and A3

The acids A1-A3 were synthesized by following procedures described elsewhere. $^{[8c,\,19,\,20]}$

Preparation of the hydrogen-bonded complexes

Before the preparation of the mixtures, the pure components were dissolved in CH_2Cl_2 , filtered, and the solvent was evaporated. The hydrogen-bonded complexes were prepared from a CH_2Cl_2 solution of a mixture of $T3C_4$ and the corresponding carboxylic acid in a 1:3 proportion. The solvent was evaporated by stirring at RT, and the mixtures were heated to their isotropic states and then cooled to RT before being used for further experiments.

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