Hydrogen Bonded Supramolecular Liquid Crystalline Complex of 2,4,6-Triarylamino-1,3,5-triazines with Semiperfluorinated Benzoic Acids

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Hydrogen bonded supramolecular complexes of 2,4,6-triarylamino-1,3,5-triazines (**T*n***) with semiperfluorinated benzoic acids have been prepared. The mesophase behaviors of such complexes were investigated with POM (polarized optical microscopy), DSC (differential scanning calorimetry) and X-ray diffraction. Columnar mesophase was found in the equimolar mixtures of the triazines with the semiperfluorinated benzoic acids. While the equimolar mixture of triazines with the nonfluorinated three fold alkoxy-modified carboxylic acid was not mesogen. The mesophase formation is analyzed as the hydrogen bonding between the **T*n*** and benzoic acid which leads to discrete dimeric supermolecule and enhances the polarity of the core region of the dimeric supermolecule; simultaneously, an increased intramolecular polarity contrast upon replacing alkyl chains by semiperfluorinated chains, which favors a microsegregation, and leads to the fromation of the columnar phase.

Keywords　hydrogenbonding, perfluorinated chains, liquid crystals

Introduction

Hydrogen bonding and π-π interactions are frequently employed as driving forces to give well-defined supramolecular architectures. Melamine (2,4,6-triarylamino-1,3,5-triazines) and its derivatives, which can involve both types of interactions, have provided a variety of elegant approaches to design new types of soft materials. Columnar mesophases formed by such compounds have been found holding potential application for electronic devices, such as (semi)conducting and photoconducting materials and chemical sensors, due to its high charge carrier mobility along the columnar axes.

Perfluorinated alkylchains are incompatibility with polar, aliphatic and aromatic segments, they have larger cross-sectional area in comparison to aliphatic chains, and distinct conformational properties, it is possible to use such fluorophobic effect to stabilize and even to modify the smectic, columnar and cubic mesophases.

Considering the special roles of both the 2,4,6-triarylamino-1,3,5-triazines and perfluorinated segment in supramolecular chemistry, we have decided to investigate the mesogenic behaviors of hydrogen bonded complex of alkoxy-substituted triarylmelamines with complementary semifluorinated benzoic acids **AF**. Additionally, to elucidate the influence of the fluorinated segments, mixtures of the triarylmelamines with the nonfluorinated three-chain benzoic acid **AC3** were also investigated. As far as we know, reports regarding mesomorphic H-bonded complexes derived from two complementary components and incorporating perfluorinated chains are restricted only to mixtures of fluorinated acids and pyridine derivatives, as well as mixtures of fluorinated acids and 2,4-diamino-6-phenyl-1,3,5-triazines.[4h,4i,]

Results and discussion

Materials and methods

The alkoxy-substituted triarylmelamines (**T12**, **T14** and **T18**) were prepared by the reaction of the corresponding alkoxy-substituted anilines with cyanuric chloride using potassium carbonate as the base in 2-butanone. The synthesis involved the preparation of alkoxy-substituted anilines by reduction of the corresponding nitro compounds with Fe-NH_4Cl.

Synthesis of (perfluoro)alkoxy benzoic acids

Synthesis of (perfluoro)alkoxy benzoic acids has been described in detail previously.[4h,9] The binary mixed systems were prepared as follows: the solvent of the solution of equimolar amount of triazine (**T12**, **T14** or **T16**) and benzoic acids (**A3**, **AF2**, **AF3** or **AC3**) in

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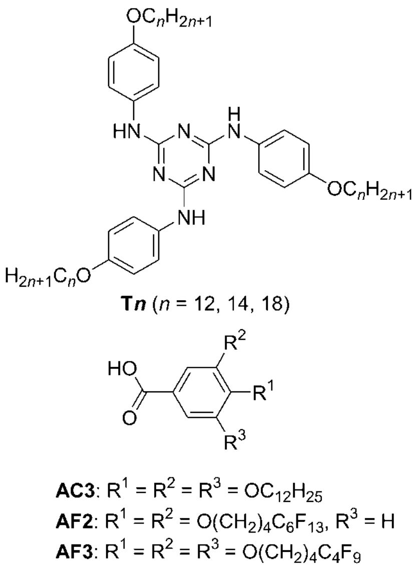
THF was evaporated and the material was heated to the isotropic state, then a dimeric complex consisting of both species linked through H-bonding was obtained. All the mixtures gave rise to homogeneous materials, providing evidence for the formation of a complex.

The formation of the mixed complex is readily deduced from infrared spectra. The infrared spectra of the separate components (triazine and acid), and that of the corresponding mixture were recorded from KBr pellets. As a representative example, the infrared spectra of **T14**, **AF2** and their complex **T14/AF2** (1/1) are shown in Figure 1. A clear change in the characteristic carbonyl bands is observed among the pure components and the mixture. Two C=O stretching bands appear in the acid and they correspond to the dimeric form (1650 cm^{-1}) and to the nonassociated form (1705 cm^{-1}) of acid respectively. After H-bonding association with the triazine, however, these bands merge to give a single peak at 1668 cm^{-1}, which corresponds to the associated triazine-carboxylic acid. Changes in the region from 3400 to 2400 cm^{-1} are also significant. **T14** shows sharp bands within the region between 3500 to 3000 cm^{-1}, which gives a much simple broad bond corresponding to the H-bonded N stretching band in the mixture, and the broad COOH bond (3400—2400 cm^{-1}) in the acid disappeared in the mixture. All these indicate the formation of the hydrogen bonded complex. The chemical structure of the complex **T14/AF2** is also confirmed by ^{1}H NMR (see experimental section).

Scheme 1 Chemical structures of the 2,4,6-triarylamino-1,3,5-triazines and the complementary semiperfluorinated benzoic acids



AC3: R^1 = R^2 = R^3 = OC$_{12}$H$_{25}$
AF2: R^1 = R^2 = O(CH$_2$)$_4$C$_6$F$_{13}$, R^3 = H
AF3: R^1 = R^2 = R^3 = O(CH$_2$)$_4$C$_4$F$_9$

Mesophase behavior

The liquid crystalline properties of separate components and the mixtures were investigated by POM and DSC, and X-ray investigation were made for selected samples. Their mesophase behaviors are summarized in Table 1.

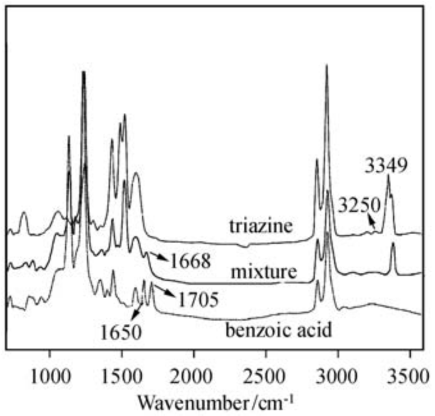


Figure 1 FTIR spectra of the pure triazine (**T14**), equimolar mixture (**T14/AF2**) and acid **AF2**.

Table 1 Mesophase, phase transition temperature and enthalpy change (in bracket) of pure compounds **T*n*** and equimolar compositions of **T*n*** with the benzoic acids **A**

Sample	Transition temperature (*T*/℃) and enthalpy change [Δ*H*/(J•g^{-1})]
T12	Cr 114 SmA 121 Iso^a
T14	Cr 121 SmA 126 Iso^a
T18	Cr 116 SmA 127 Iso^a
T12/AC3	Cr 81 Iso^a
T12/AF2	Cr 48 (17.3) Col 110 (0.5) Iso^b
T12/AF3	Cr 55 (0.9) Col 144 (2.8) Iso^b
T14/AC3	Cr$_1$93 (21.2) Cr$_2$104 (32.9) Iso^b
T14/AF2	Cr 47 (4.5) Col 117 (0.7)Col 131 (0.1) Iso^b
T14/AF3	Cr 54 (6.2) Col 139 (3.6) Iso^b
T18/AC3.	Cr 114 Iso^a
T18/AF2	Cr 67 (13.3)Cr 102 (33.0) Col 134 (6.5) Iso^b
T18/AF3	Cr 43 (12.9) Cr 63 (5.6) Col 117 (1.8) Iso^b

^{a} Transition temperature was determined by POM; ^{b} Transition temperature and enthalpy changes were determined by DSC (peak temperature, first cooling scan, 5 ℃•min^{-1}).

All alkoxy substituted triarylmelamines **T*n*** show smectic A phase, which is characterized by texture, consisting of both focal-conic and pseudo isotropic regions (Figure 2a). The occurrence of focal-conic fans suggests a layered structure, whereas the pseudo isotropic region indicates an on average orthogonal organization of the molecules with respect to the layer planes. With the elongation of the alkoxy chains, an increase of both the melting and clear temperatures is observed. The formation of the smectic A phase can be explained with the model shown in Figure 2d. The triazines are suspected to form H-bonding dimmers, in which the six periperial alkoxy chains are located in both side of the rigid core consisted by the N—H···N hydrogen bonded aromatic cores, to form layer structure.

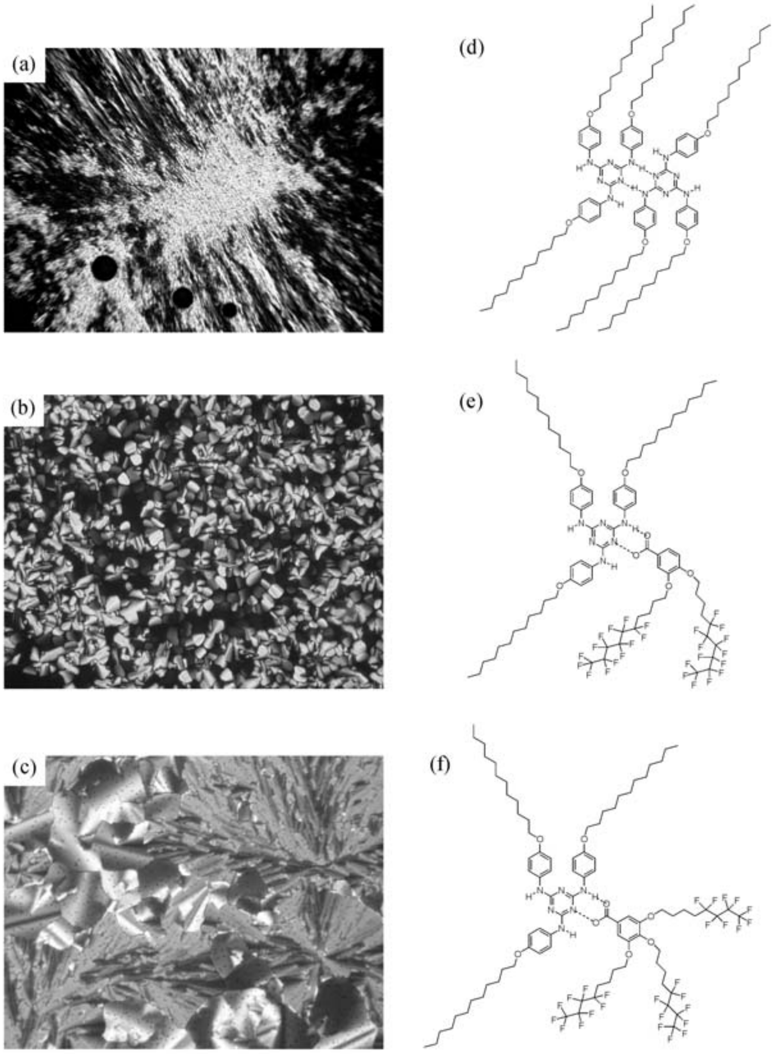


Figure 2 (a) Smectic A phase of compound **T14** at 121 ℃ under POM; (b) columnar phase of binary mixture of **T14/AF2** at 117 ℃ under POM; (c) columnar phase of binary mixture of **T14/AF3** at 139 ℃ under POM; (d) model showing the organization of the molecules in the smectic A phase of compound **T14**; (e) model showing the organization of the molecules in the columnar phase of binary mixture of **T14/AF2**; (f) model showing the organization of the molecules in the columnar phase of binary mixture of **T14/AF3**.

H-Bonded complexes tiazine (T*n*)/benzonic acid (AF2, AF3 or A3) (1/1)

Each investigation of binary 1∶1 mixture of the triazines **T*n*** with the semiperfluorinated benzoic acids (**AF2** or **AF3**) exhibits columnar mesophase, as shown by their typical spherulitic textures with homotropic aligned regions containing birefringent filamens under POM (Figures 2b, 2c).

The binary 1∶1 mixture of **T*n*** with the three fold semifluorinated chain substituted benzoic acids (**AF3)** is much border than the corresponding binary 1∶1 mixture of benzoic acid with two semiflurinated chains (**AF2**). This means, with increasing degree of fluorination, the fluorophobic effect and the intramolecular contrast increased and thus forces micro-segregation, which can efficiently be used to dramatically stabilize the mesophases.

We have made the X-ray investigation on the binary mixture of triazine **T14** with semifluorinated benzoic acids **AF2** and **AF3,** respectively. Unfortunately for both samples, there is only one reflex together with a weak second order reflex and it was not possible to obtain aligned samples. We have tentatively indexed it to square or hexagonal (Figure 3, Table 2) columnar phase.

The texture appears to be uniaxial and therefore a rectangular or oblique lattice is unlikely. Simultaneously the texture clearly indicates a columnar phase (Figures 2b and 2c), hence smectic phase can be excluded. As the hexagonal phase is found more frequently than square phase, columnar hexagonal phase appears to be the most likely phase for **T14/AF2** and **T14/AF3**.

On the contrary, all the equimolar mixtures of **T*n*** with the nonfluorinated three fold alkoxy-modified carboxylic acid **AC3** show a single melting transition. However, no mesomorphic properties can be found in the mixed system **T*n*/AC3**.

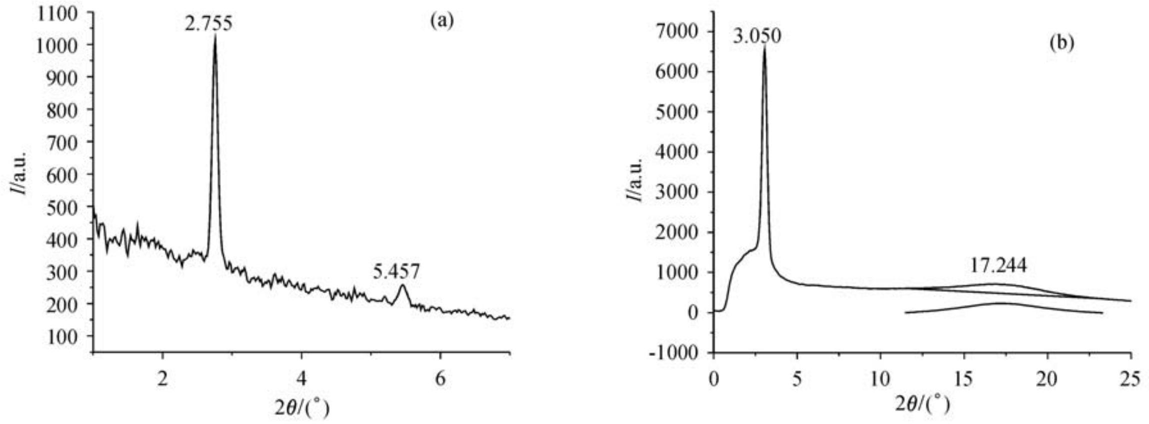


Figure 3 WAXS (wide angle X-ray scattering) diffraction patterns of $\mathrm{Col_{hex}}/p6mm$ (or $\mathrm{Col_{squ}}/p4mm$) phase of binary mixture of **T14/AF2** at 90 ℃ (a) and 140 ℃ (b).

Table 2 X-ray data of binary mixtures of **T14/AF2** and **T14/AF3**

Sample	T/℃	Phase group	$2\theta_{\mathrm{obs}}$/(°)	d_{obs}/nm	hk	Parameter/nm
T14/AF2	90	$\mathrm{Col_{hex}}/p6mm$ (or $\mathrm{Col_{squ}}/p4mm$)	2.7550	3.2068	10	$a_{\mathrm{hex}}=3.7$ (or $a_{\mathrm{squ}}=3.2$)
			5.4570	1.6194	20	
T14/AF3	140	$\mathrm{Col_{hex}}/p6mm$ (or $\mathrm{Col_{squ}}/p4mm$)	3.0500	2.8967	10	$a_{\mathrm{hex}}=3.45$ (or $a_{\mathrm{squ}}=2.9$)
			17.2440	0.5142	11	

The hydrogen bonding between the triazines **T*n*** and benzoic acids predominantly leads to discrete dimeric supermolecules (Figures 2e, 2f). The hydrogen bonding enhances the polarity of the core region of the dimeric supermolecules. Simultaneously, the nonpolar nature of molecular periphery is enhanced by introducing the non-polar alkyl (or semifluorinated) chains of the acid components. The nonappearance of mesomorphic behavior for the mixtures **T*n*/AC3** very distinctly illustrated the enhanced mesophase structure formation tendencies obtained by replacing the alkyl groups of the benzoic acid components by semifluorinated chains.

Conclusion

A new family of hydrogen bonded supramolecular liquid crystalline complex of melamine (2,4,6-triarylamino-1,3,5-triazines) with semiperfluorinated benzoic acids has been obtained. Columnar mesophases are found in these binary 1∶1 mixtures of the triazine **T*n*** with the semiperfluorinated benzoic acids **AF2** or **AF3**. While the equimolar mixtures of **T*n*** with the non-fluorinated three fold alkoxy-modified carboxylic acid **AC3** are non mesogens. The mesophase formation is essentially due to an increased intramolecular polarity contrast upon replacing alkyl chains by semiperfluorinated chains, which favors a microsegregation.

Experimental

Apparatus and materials

Reactions require an inert gas atmosphere, so they were conducted under argon and the glassware was oven-dried (140 ℃). Commercially available chemicals were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-DRX-500 spectrometer. Mass spectra were recorded on a Finnigan MAT 90 spectrometer at an ionization potential of 70 eV. Microanalysis was performed using a Leco CHNS-932 elemental analyzer. IR (KBr) spectra were recorded on a Nicolet AVATAR 360 infrared spectrophotometer. Column chromatography was performed with silica gel 60 (230—400 mesh) from Merck. Transition temperatures were measured by means of a Nikon Optiphot polarizing microscope with Linkam LTS 350 hotstage and control unit and confirmed using differential scanning calorimetry (Perkin Elmer DSC-7). X-ray investigations were carried out with a Guinier-Goniometer (Huber).

Preparation

3,4,5-Tris-dodecyloxy-benzoic acid was prepared according to literature, m.p. 59 ℃ (Lit.[9] 60 ℃). Perfluoroalkoxy benzoic acids were synthesized according to reference.[4h]

3,4-Bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorodecyl-1-oxy)benzoic acid (9-H4F6) Transitional temperature: Cr 57 Col 82 Iso; IR (KBr) *v*: 3300 (OH), 2915, 2853 (CH_2, CH_3), 1705, 1650 (C=O), 1596, 1416, 1336 (C=C), 1272, 1224, 1128, 1048 (C—O—C), 877, 824, 748 (=CH, ArH) cm^{-1}.

3,4,5-Tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorooctyl-1-oxy)benzoic acid (10-H4F4) Cr 43 (Col 34) Iso.

General procedure for etherification

Under an argon atmosphere, a mixture of nitrophenol (8 mmol), K_2CO_3 (24 mmol) and *n*-bromoakane (12 mmol) in acetone (50 mL) was heated under reflux overnight. Ethyl acetate (50 mL) and water (50 mL) were added, the organic layer was separated, dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. The rude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate, V∶V＝10∶1). Colorless crystal (yield 82%—85%).

1-(Dodecyloxy)-4-nitrobenzene m.p. 54 ℃ (Lit.[10] 55 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.88 (t, *J*＝6.8 Hz, 3H, CH_3), 1.27—1.85 (m, 20H, 10CH_2), 4.05 (t, *J*＝6.5 Hz, 2H, OCH_2), 6.94 (d, *J*＝9.2 Hz, 2H, ArH), 8.20 (d, *J*＝9.2 Hz, 2H, ArH).

1-Nitro-4-(tetradecyloxy)benzene m.p. 59 ℃ (Lit.[11] 57—60 ℃).

1-Nitro-4-(octadecyloxy)benzene m.p. 71 ℃ (Lit.[12] 71—72 ℃).

Synthesis of the alkoxysubstituted anilines 3/*n*

A mixture of ammonium chloride (0.8 mmol) and iron powder (6 mmol) in water (10 mL) was heated under reflux for 5 min. Then the corresponding nitro compound was added and the solution was refluxed for 3 h. Afterwards, saturated aqueous Na_2CO_3 solution was added, the mixture was stirred for 30 min at 40 ℃ and extracted with $CHCl_3$. The combined organic extracts were dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. The rude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate, V∶V＝5∶1). Yields of **3/12**, **3/14** and **3/18** were 68%, 70% and 68%, respectively.

4-(Dodecyloxy)benzenamine (3/12) m.p. 51 ℃ (Lit.[13] 51 ℃); ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.88 (t, *J*＝6.6 Hz, 3H, CH_3), 1.26—1.75 (m, 20H, 10CH_2), 3.88 (t, *J*＝6.5 Hz, 2H, OCH_2), 6.64 (d, *J*＝8.7 Hz, 2H, ArH), 6.74 (d, *J*＝8.6 Hz, 2H, ArH).

4-(Tetradecyloxy)benzenamine (**3/14**) m.p. 66 ℃ (Lit.[14] 65—68 ℃).

4-(Octadecyloxy)benzenamine (**3/18**) m.p. 64 ℃ (Lit.[12] 64 ℃).

General procedure for the preparation of alkoxy-substituted triarylmelamine T*n*

Under an argon atmosphere, a mixture of cyanuric chloride (0.5 mmol), K_2CO_3 (2 mmol) and appropriate alkoxysubstituted anilines (**3/12**, **3/14**, **3/18**) (2 mmol) in 2-butanone (20 mL) was heated under reflux for 3 d. Chloroform and water were added, the organic layer was separated, dried over $MgSO_4$, and the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (eluent: petroleum ether/ethyl acetate, V∶V＝10∶1). Yields of **T12**, **T14** and **T18** were 71%, 68% and 64%, respectively.

N^2,N^4,N^6-Tris(4-(dodecyloxy)phenyl)-1,3,5-triazine-2,4,6-triamine (T12) ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.88 (t, *J*＝6.5 Hz, 9H, 3CH_3), 1.26—1.79 (m, 60H, 30CH_2), 3.94 (t, *J*＝6.5 Hz, 6H, 3OCH_2), 6.85 (d, *J*＝8.5 Hz, 6H, ArH), 7.42 (d, *J*＝8.8 Hz, 6H, ArH); IR (KBr) *v*: 3351, 3253 (NH), 2918, 2850 (CH_2, CH_3), 1616 (C＝N), 1596, 1516, 1416 (C＝C), 1225, 1228, 1049 (C—O—C), 816 (＝CH, ArH) cm^{-1}; MS (70 eV) *m/z* (%): 907.7 (M＋1, 100). Anal. calcd for $C_{57}N_{90}N_6O_3$: C 75.45, H 10.00, N 9.26; found C 75.05, H 9.78, N 9.58.

N^2,N^4,N^6-Tris(4-(tetradecyloxy)phenyl)-1,3,5-triazine-2,4,6-triamine (T14) ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.88 (t, *J*＝6.9 Hz, 9H, 3CH_3), 1.26—1.79 (m, 72H, 36CH_2), 3.94 (t, *J*＝6.5 Hz, 6H, OCH_2), 6.85 (d, *J*＝8.5 Hz, 6H, ArH), 7.42 (d, *J*＝8.8 Hz, 6H, ArH); IR (KBr) *v*: 3349, 3250 (NH), 2916, 2852 (CH_2, CH_3), 1614 (C＝N), 1596, 1516, 1416 (C＝C), 1224, 1228, 1048 (C—O—C), 814 (＝CH, ArH) cm^{-1}; MS (70 eV) *m/z* (%): 991.8 (M＋1, 100). Anal. calcd for $C_{63}N_{102}N_6O_3$: C 76.31, H10.37, N 8.48; found C 76.71, H 10.14, N 8.65.

N^2,N^4,N^6-Tris(4-(octadecyloxy)phenyl)-1,3,5-triazine-2,4,6-triamine (T18) ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.88 (t, *J*＝6.9 Hz, 9H, 3CH_3), 1.26—1.79 (m, 96H, 48CH_2), 3.94 (t, *J*＝6.5 Hz, 6H, OCH_2), 6.85 (d, *J*＝8.5 Hz, 6H, ArH), 7.42 (d, *J*＝8.8 Hz, 6H, ArH); IR (KBr) *v*: 3350, 3249 (NH), 2919, 2852 (CH_2, CH_3), 1613 (C＝N), 1595, 1514, 1417 (C＝C), 1227, 1229, 1050 (C—O—C), 818 (＝CH, ArH) cm^{-1}; MS (70 eV) *m/z* (%): 1160.0 (M＋1, 100). Anal. calcd for $C_{75}N_{126}N_6O_3$: C 77.67, H 10.95, N 7.25; found C 77.93, H 10.74, N 7.03.

T14/AF2 The solvent of the solution of equimolar amounts of triazine (**T12**, **T14** or **T16**) (0.05 mmol) and benzoic acids (**A3**, **AF2** or **AF3**) (0.05 mmol) was evaporated and the material heated to the isotropic state, a dimeric complex consisting of both species linked through H-bonding was obtained. All the mixtures gave rise to homogeneous materials, providing evidence for the formation of a complex.

As an example, the NMR date of complex **T14/AF2**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.88 (t, *J*＝6.8 Hz, 9H, 3CH_3), 1.26—2.22 (m, 84H, 42CH_2), 3.94 (t, *J*＝6.6 Hz, 6H, 3OCH_2), 4.10 (t, *J*＝5.3 Hz, 4H, 2OCH_2), 6.86 (d, *J*＝8.4 Hz, 6H, ArH), 6.89 (d, *J*＝8.6 Hz, 1H, ArH), 7.44 (d, *J*＝8.8 Hz, 6H, ArH), 7.59 (s, 1H, ArH), 7.74 (d, *J*＝8.4 Hz, 1H, ArH); IR (KBr) *v*: 3320 (NH···O＝C—OH), 2915, 2853 (CH_2, CH_3), 1668 (C＝O), 1613 (C＝N), 1596, 1416 (C＝C), 1224, 1128, 1048 (C—O—C), 878, 814,749 (＝CH, ArH) cm^{-1}.

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