# Hydrogen-Bonded Mesomorphic Complexes Combining Hydrophilic and Fluorophilic Molecular Segments

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## Supporting Information

### Instrumental

Texture observations were made using an Olympus BHS polarizing microscope in conjunction with a Linkam TMH/S 600 hot stage and a Linkam TP 92 control unit. Photo micrographs were obtained with an Olympus E20 digital mirror reflex camera. Calorimetric investigations were performed with a Netzsch DSC 200. Temperature depending IR spectroscopy was performed with a Digilab Scimitar FTS 2000 Series FT-IR spectrometer fitted with a Golden Gate Mk II ATR system (Specac Ltd., England). XRD patterns were recorded with Ni filtered and pin-hole collimated Cu-$K_\alpha$ radiation; usual exposure time was 15 min. A small droplet of the compound was slowly cooled on a glass plate (rate: 0.1 K $min^{-1}$) on a temperature-controlled heating stage and the sample detector distance was 10.15 cm. Diffraction patterns were recorded with a 2D detector (Vantec 500, Bruker). Photographs of CPK models were obtained with a Nikon D50 digital mirror reflex camera.

**Table S1.** Small angle X-ray diffraction data for the hexagonal columnar ($Col_h$) mesophases of the binary (1:3) mixtures and (1:1) mixtures of the (oligo)ethylene glycol substituted diaminotriazine **1** with the two-chain and three-chain partially fluorinated benzoic acids **2-[$F_xC_y$]** and **3-[$F_xC_y$]**.

| Mixture | Scattering angle ($2\theta$) | Reflections / nm | | Miller indices ($hkl$) | Lattice constants ($a_{hex}$ / nm) |
|---|---|---|---|---|---|
| | | $d_{obs}$ | $d_{calc}$ | | |
| **(1:3) 1/2-[$F_6C_4$]** | 3.206 | 2.76 | - | 100 | 3.18 |
| **(1:3) 1/3-[$F_6C_4$]** | 3.188 | 2.77 | - | 100 | 3.20 |
| **(1:3) 1/3-[$F_6C_6$]** | 2.985 | 2.96 | - | 100 | 3.42 |
| | 5.149 | 1.72 | 1.71 | 110 | |
| | 5.944 | 1.49 | 1.48 | 200 | |
| **(1:1) 1/2-[$F_6C_4$]** | 2.902 | 3.04 | - | 100 | 3.51 |
| | 5.041 | 1.75 | 1.75 | 110 | |
| | 5.818 | 1.52 | 1.52 | 200 | |
| **(1:2) 1/2-[$F_6C_4$]** | 3.00 | 2.94 | - | 100 | 3.40 |
| | 5.18 | 1.71 | 1.70 | 110 | |
| | 5.99 | 1.47 | 1.47 | 200 | |
| **(1:1) 1/3-[$F_6C_4$]** | 3.068 | 2.88 | - | 100 | 3.33 |
| | 6.135 | 1.44 | 1.44 | 200 | |
| | 8.027 | 1.10 | 1.09 | 210 | |
| **(1:1) 1/3-[$F_6C_6$]** | 2.902 | 3.04 | - | 100 | 3.51 |
| | 5.037 | 1.75 | 1.75 | 110 | |
| | 5.841 | 1.51 | 1.52 | 200 | |

**Table S2.** Calculations of the molecular volume ($V_{mol}$), volume of the hypothetical unit cells ($V_{cell}$) and number of [1:2] or [1:3] triazine/acid adducts in these unit cells ($n_{cell}$).

| Mixture | $V_{cell}$ (nm$^3$) | $V_{mol}$ (nm$^3$) | $n_{cell}$ | triazine/acid adduct |
|---|---|---|---|---|
| **(1:3) 1/2-[$F_6C_4$]** | 3.941 | 2.935 | 1.34 | [1:3] |
| **(1:3) 1/3-[$F_6C_4$]** | 3.991 | 3.937 | 1.01 | [1:3] |
| **(1:3) 1/3-[$F_6C_6$]** | 4.558 | 4.045 | 1.13 | [1:3] |
| **(1:1) 1/2-[$F_6C_4$]** | 4.802 | 2.114 | 2.27 | [1:2] |
| | 4.802 | 3.736 | 1.28 | [1:4] |
| **(1:2) 1/2-[$F_6C_4$]** | 4.505 | 2.114 | 2.13 | [1:2] |
| **(1:1) 1/3-[$F_6C_4$]** | 4.321 | 3.937 | 1.10 | [1:3] |
| **(1:1) 1/3-[$F_6C_6$]** | 4.802 | 4.045 | 1.19 | [1:3] |

$V_{cell}$ = volume of the unit cell defined by the dimensions $a^2$ x sin(60°) x 0.45 nm for hexagonal phases;
$V_{mol}$ = volume for a single triazine/acid adduct as calculated using the crystal volume increments;[1]
$n_{cell}$ = number of adducts in the unit cell, calculated according to $n_{cell} = V_{cell}/V_{mol}$.

**Table S3.** Calculation of the amount of phase-separated pure triazine **1** in equimolar mixtures with the fluorinated benzoic acids **2-[$F_xC_y$]** and **3-[$F_xC_y$]**[a].

| Mixture | Transition temperature (°C) / Transition enthalpy (kJ/mol) | Phase separated triazine **1** |
|---|---|---|
| **(1:1) 1/2-[$F_6C_4$]** | 85.9 / 2.78 | 28.4% |
| **(1:2) 1/2-[$F_6C_4$]** | 84.9 / 0.94 | 9.6% |
| **(1:1) 1/3-[$F_6C_4$]** | 84.8 / 1.44 | 14.7% |
| **(1:1) 1/3-[$F_6C_6$]** | 85.2 / 2.19 | 22.4% |

[a] The content of uncomplexed triazine **1** in the (1:1) mixtures was calculated from the enthalpy values of the phase transition Iso → IC* (DSC 2$^{nd}$ cooling); the appropriate value obtained for the pure triazine (85.5°C / 9.8 kJ/mol) was used as reference and set to 100%.

**Supplementary figures**

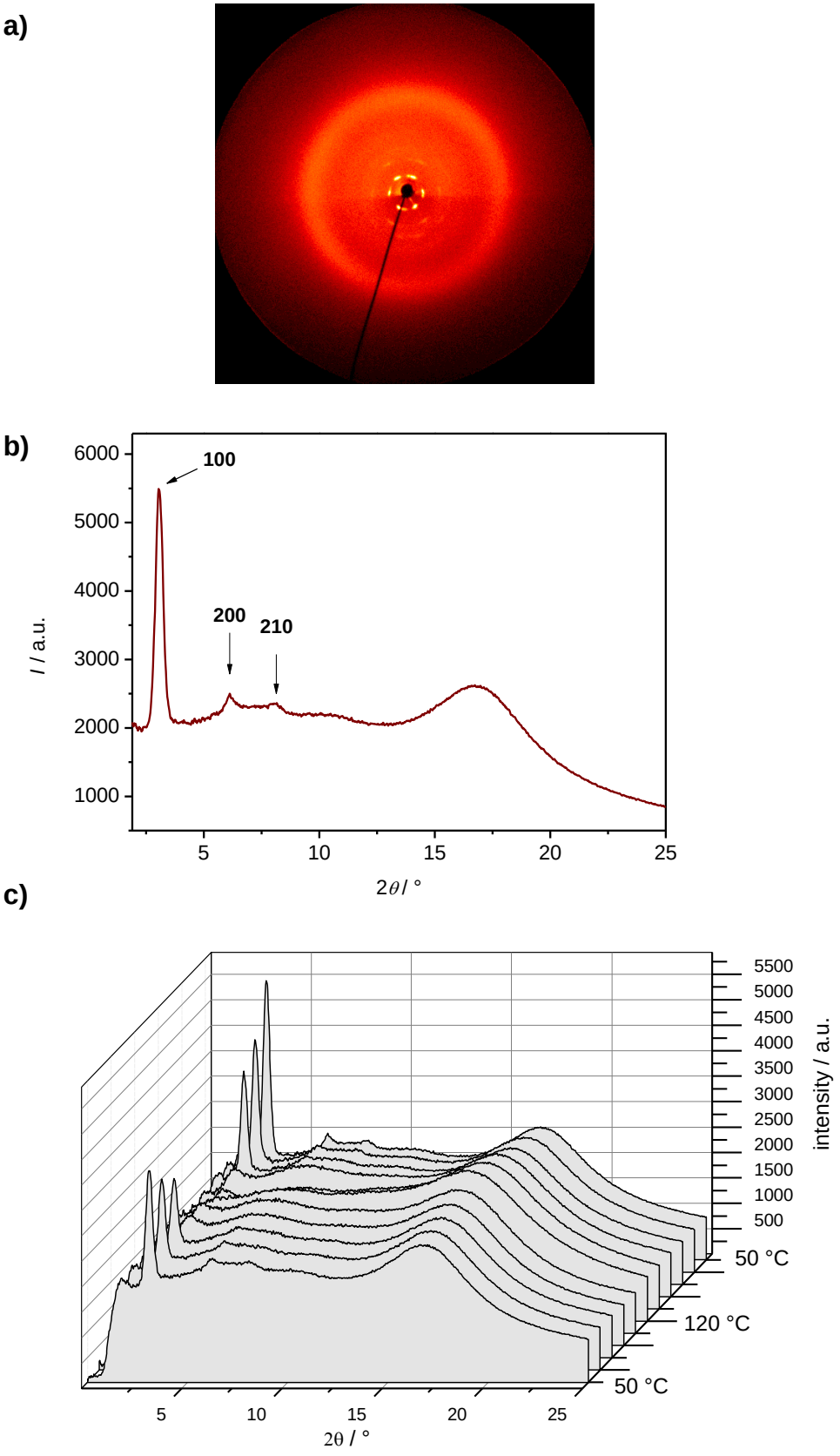
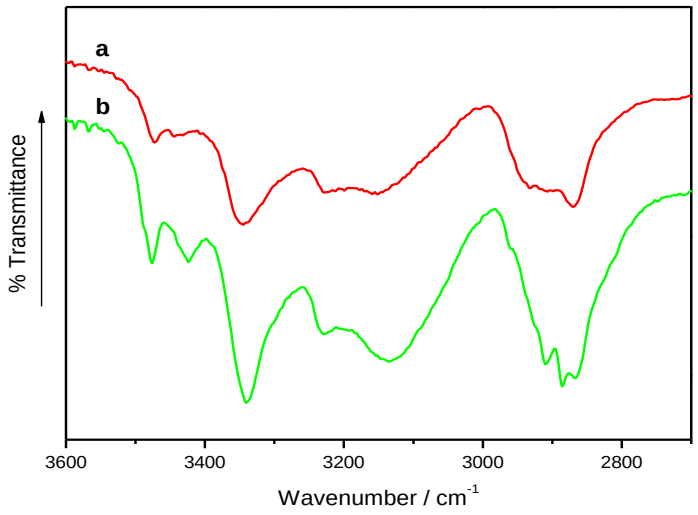



**Figure S1.** (a) XRD pattern of a surface aligned sample of the (1:1) mixture **1/3-[$F_6C_4$]** at 50°C; (b) 2θ scan over this pattern; (c) Temperature depending XRD pattern of the equimolar mixture **1/3-[$F_6C_4$]**.

A)




B)

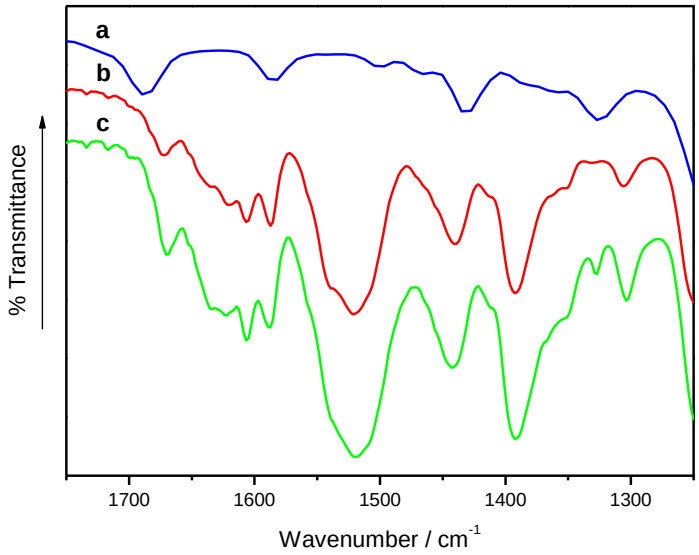



**Figure S2.** FT IR spectra on cooling at 50°C. (A) Spectral range from 2700 to 3600 $cm^{-1}$ of (a) the (1:1) mixture **1/3-[$F_6C_6$]**; (b) the pure diaminotriazine **1**. (B) region between 1250 and 1750 $cm^{-1}$ of (a) the pure benzoic acid **3-[$F_6C_6$]**; (b) the (1:1) mixture **1/3-[$F_6C_6$]**; (c) the pure diaminotriazine **1**.

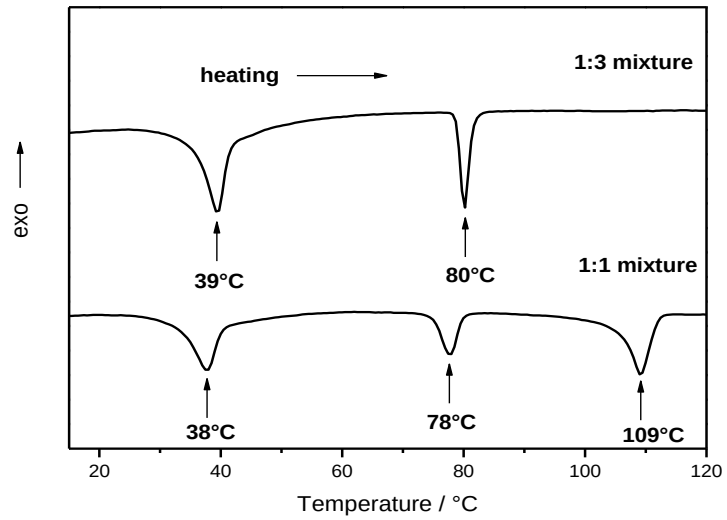



**Figure S3.** DSC traces (2nd heating with 10 K/min) of the (1:1) and (1:3) mixtures **1/3-[$F_6C_4$]** in comparison.

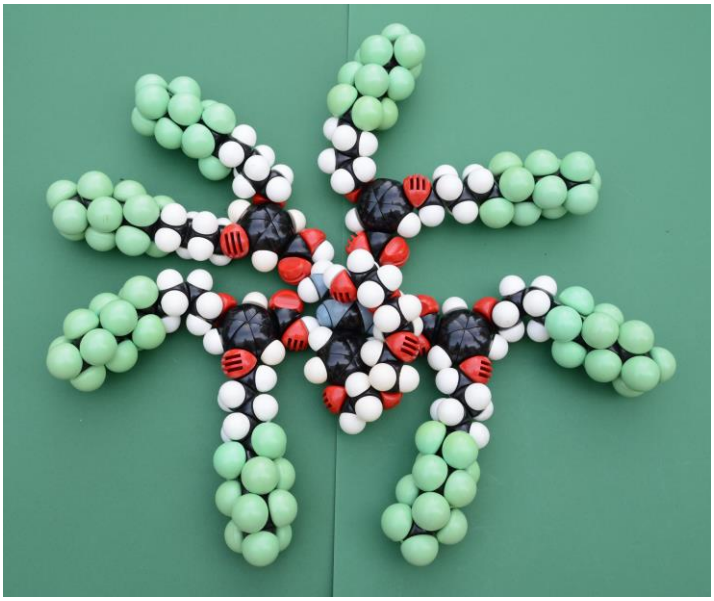


**Figure S4.** CPK model showing a [1:4] aggregate of the oligo(ethylene oxide) substituted diaminotriazine **1** with four molecules of the two-chain partially fluorinated benzoic acid **2-[$F_6C_4$]** with a pronounced circular shape.

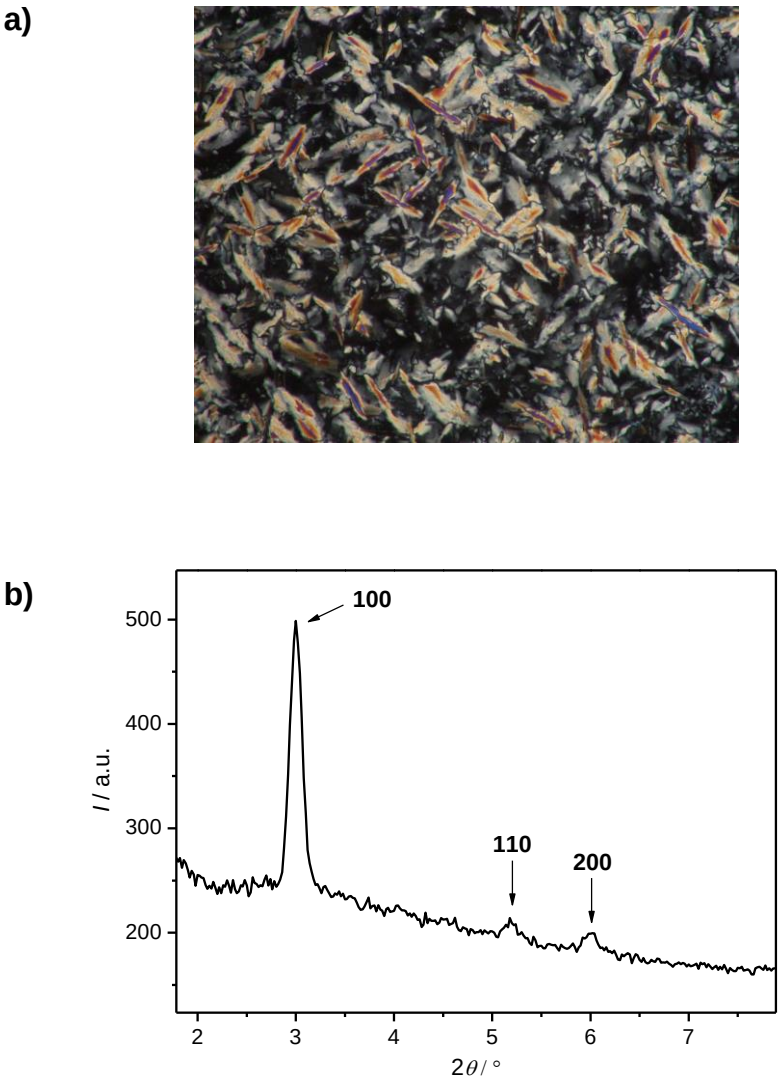



**Figure S5.** (a) Optical texture observed for the hexagonal columnar phase of the (1:2) **1/2-[$F_6C_4$]** mixture; (b) SAXS diffractogram of the $Col_h$ phase of the (1:2) mixture **1/2-[$F_6C_4$]** at 50°C.

1 A. Immirzi, B. Perini, *Acta Crystallogr. Sect. A* **1977**, *33*, 216-218.