Supporting Information

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Easily Accessible Thermotropic Hydrogen-Bonded Columnar Discotic Liquid Crystals from Fatty Acid–Tris-Benzimidazolyl Benzene Complexes

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open_201600078_sm_misellaneous_information.pdf
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1. $^1$H-NMR and elemental analysis of templates with different purities

TBIB, crude

![NMR spectrum of TBIB, crude](image1)

ESI 1: $^1$H-NMR ($d_6$-DMSO) of TBIB after the reaction, precipitated from water. The purity at this point was unsatisfactory, the integrals did not match with the expected values.

TBIB, crystallized from methanol

![NMR spectrum of TBIB, crystallized](image2)

ESI 2: $^1$H-NMR ($d_6$-DMSO) of TBIB after being precipitated from water followed by a crystallization from MeOH. A minor improvement was observed, the integrals increased from 1.46 to 1.58 for the right two signals.

TBIB, sublimed

![NMR spectrum of TBIB, sublimed](image3)

ESI 3: $^1$H-NMR ($d_6$-DMSO) of TBIB after precipitation from water followed by a sublimation step. The integration matches with the expected values of the product.
| Sample                             | Carbon | Hydrogen | Nitrogen |
|-----------------------------------|--------|----------|----------|
| Calculated\(\ast\)              | 76.04  | 4.25     | 19.71    |
| Crude product (purple)            | 54.07  | 3.69     | 13.86    |
| Crystallized from MeOH            | 71.67  | 4.26     | 18.42    |
| **After sublimation**             | **75.88** | **4.06** | **19.42** |

**ESI 4**: Elemental analysis of three different grades of TBIB. Only the sublimated product had all three elements within 0.4 % of the calculated values.
2. POM micrographs of different compositions

**TBIB + dodecanoic acid**

| 2.95 eq. | 3.00 eq. | 3.05 eq. | 3.10 eq. |

**MeTBIB + dodecanoic acid**

| 2.83 eq. | 2.91 eq. | 2.94 eq. | 2.99 eq. |

**TBIB + n-DFA**

| 1.70 eq. | 1.75 eq. | 1.80 eq. |

ESI S: POM micrographs (in grayscale) of the isotropic phase of fatty acids mixed with increasing amounts of TBIB or MeTBIB. The first row shows when dodecanoic acid is mixed with TBIB at different ratios. The second row shows the isotropic phase when MeTBIB is used, which is free from residue even when only 2.94 equiv. of dodecanoic acid is used. The third row shows mixtures of dimerized linoleic acid and TBIB. 1.75 equiv. of n-DFA is required to form a homogeneous isotropic phase.
3. Azimuthally integrated XRD diffractograms of dodecanoic acid, TBIB and MeTBIB

**ESI 6:** X-Ray diffractogram (wide angle) of dodecanoic acid at 33 °C and 58 °C.

**ESI 7:** X-Ray diffractogram (wide angle) of TBIB at 126 °C.

**ESI 8:** X-Ray diffractogram (wide angle) of MeTBIB at 126 °C.
4. Transition temperatures and latent heats as a function of equivalents of dodecanoic acid and hexadecanoic acid mixed with TBIB

**ESI 9**: Clearing temperature and the accompanying latent heat determined from the heating run of TBIB mixed with different equiv. dodecanoic acid. Above 3.1 equiv. the transition temperature starts to drop. The latent heat does not show a clear trend.

**ESI 10**: Clearing temperature and the accompanying latent heat determined from the cooling run of TBIB mixed with different equiv. dodecanoic acid. At 3.1 equiv. a maximum for the transition temperature is observed. The latent heat does not show a clear trend.
**ESI 11:** Clearing temperature and the accompanying latent heat determined from the heating run of TBIB mixed with different equiv. hexadecanoic acid. Above 3.1 equiv. the transition temperature starts to drop, above 3.2 equiv. the transitions could not be observed anymore.

**ESI 12:** Clearing temperature and the accompanying latent heat determined from the cooling run of TBIB mixed with different equiv. hexadecanoic acid. Above 3.1 equiv. the transition temperature starts to drop. A similar trend is observed from the latent heat of the transition, however, above 3.2 equiv. integration of the latent heat becomes ambiguous because of the broadness of the transition.
5. POM micrographs of different fatty acids mixed with TBIB and MeTBIB

ESI 13: Collection of POM micrographs of saturated fatty acid homologues mixed with TBIB, 3.1 equiv. of acid was used. \( \text{C}_6\text{H}_{12}\text{O}_2 \) and \( \text{C}_8\text{H}_{16}\text{O}_2 \) were difficult to handle due to evaporation of the acid. \( \text{C}_{10}\text{H}_{22}\text{O}_2 \) to \( \text{C}_{16}\text{H}_{32}\text{O}_2 \) all gave Col\text{hex} phases. \( \text{C}_{18}\text{H}_{36}\text{O}_2 \) has a different texture, which is recognized as a nematic phase. \( \text{C}_{22}\text{H}_{44}\text{O}_2 \) did not possess an LC phase.

ESI 14: Collection of POM micrographs of various acids mixed with TBIB and MeTBIB. The first row consists of mixtures of TBIB with unsaturated fatty acids, all have the typical Col\text{hex} texture. The second row is TBIB mixed with 4-methyl nonanoic acid (Col\text{hex} texture), decyl phosphonic acid [LC 1]: n.d., [LC 2]: nematic texture and 4-(2-(methacryloyloxy)ethoxy)-4-oxobutanoic acid (Col\text{hex} texture, with residual solids). The third row are mixtures of MeTBIB with dodecanoic acid (Col\text{hex} texture) and 4-dodecyl benzenesulfonic acid (Col\text{N} texture).
6. XRD diffractograms at various temperatures of octadecanoic acid mixed with TBIB

ESI 15: Temperature dependent X-ray diffractograms of octadecanoic acid (3.10 equiv.) mixed with TBIB. In the heating run it is observed that after a crystalline phase two diffractograms were measured where the \( d_{(100)} \) intensity is higher than the following temperature points, these two are indicated by the thick black line. Since the two diffractograms lack additional diffraction planes besides \( d_{(100)} \) and \( d_{(001)} \) the phase is ascribed to be Col\textsubscript{N}; \( q_1 = 0.259 \text{ Å}^{-1} \rightarrow d_{(100)}, q_2 = 1.39 \text{ Å}^{-1} \rightarrow d_{(Alkyl)}, q_3 = 1.843 \text{ Å}^{-1} \rightarrow d_{(001)}. \)
7. **Numerical values of transition temperatures and latent heats for mixtures with TBIB**

| Acid                                      | Equiv. | $T_{KtoK_2}$ [°C] | $T_{KtoLC}$ [°C] | $|\Delta H|_{KtoLC}$ [°C] (kJ/g) | $T_{LCtoIso.}$ [°C] | $|\Delta H|_{LCtoIso.}$ [°C] (kJ/g) | $T_{Iso. to LC}$ [°C] | $|\Delta H|_{Iso. to LC}$ [°C] (kJ/g) |
|-------------------------------------------|--------|-------------------|------------------|--------------------------------|---------------------|---------------------------------|-----------------------|---------------------------------|
| Hexanoic acid                             | 3.10   | -                 | 167.8            | 194.3 (9.31)                   | -                   | 186.5 (12.0)                    | -                     | -                               |
| Heptanoic acid                            | 3.10   | -                 | 134.7            | 189.0 (7.14)                   | -                   | 168.8 (5.90)                    | -                     | -                               |
| Octanoic acid                             | 3.10   | -                 | 106.6            | 182.0 (5.29)                   | -                   | 166.4 (6.28)                    | -                     | -                               |
| Decanoic acid                             | 3.10   | -                 | 94.1             | 157.1 (3.88)                   | -                   | 156.2 (1.76)                    | -                     | -                               |
| Undecanoic acid                           | 3.10   | 72.9              | 94.3             | 144.0 (2.92)                   | -                   | 142.4 (2.92)                    | -                     | -                               |
| Dodecanoic acid                           | 3.10   | 83.5              | 92.8             | 135.5 (2.33)                   | -                   | 134.0 (2.96)                    | -                     | -                               |
| Tridecanoic acid                          | 3.10   | 80.5              | 90.6             | 122.5 (1.88)                   | -                   | 121.2 (1.79)                    | -                     | -                               |
| Tetradecanoic acid                        | 3.10   | 68.6              | 83.2             | 112.8 (1.62)                   | -                   | 111.4 (1.55)                    | -                     | -                               |
| Hexadecanoic acid                         | 3.10   | 71.8              | 77.1             | 88.9 (1.01)                    | -                   | 87.5 (1.77)                     | -                     | -                               |
| Octadecanoic acid                         | 3.10   | 65.9              | 74.5             | 82.2 (0.32)                    | -                   | 66.0 (0.23)                     | -                     | -                               |
| Docosanoic acid                           | 3.10   | 73.8              | -                | -                              | 91.6                | -                               | -                     | -                               |
| Dodecanoic acid                           | 2.95   | -                 | -                | 135.4 (2.48)                   | -                   | 131.6 (3.32)                    | -                     | -                               |
| Hexadecanoic acid                         | 2.95   | -                 | -                | 88.3 (0.93)                    | -                   | 82.0 (0.78)                     | -                     | -                               |
| Oleic acid                                | 3.10   | -                 | 88.6             | 89.1 (0.31)                    | -                   | 86.9 (2.52)                     | -                     | -                               |
| Linoleic acid                             | 3.10   | -                 | 85.3             | 85.3 (0.16)                    | -                   | 80.6 (0.62)                     | -                     | -                               |
| Linolenic acid                            | 3.10   | -                 | Undetected       | -                              | -                   | 78.1 (0.88)                     | -                     | -                               |
| n-DFA                                     | 3.50   | -                 | Undetected       | -                              | -                   | 77.2 (1.37)                     | -                     | -                               |
| rac-2-methyl hexanoic acid                | 3.10   | -                 | -                | -                              | 136.1               | -                               | -                     | -                               |
| rac-2-ethyl hexanoic acid                 | 3.10   | -                 | -                | -                              | 124.9               | -                               | -                     | -                               |
| rac-2-hexyl decanoic acid                 | 3.10   | -                 | -                | -                              | 79.2                | -                               | -                     | -                               |
| (R)-citronelllic acid                     | 3.10   | -                 | -                | -                              | 93.5                | -                               | -                     | -                               |
| rac-4-methyl nnoneanoic acid              | 3.10   | -                 | 73.5             | 70.5 (5.48)                    | -                   | 169.4 (~6)                      | -                     | -                               |
| Dodecy amide                              | 3.10   | -                 | -                | -                              | -                   | -                               | -                     | -                               |
| Decyl phosphonic acid                     | 3.10   | 115.2             | 166.7            | 206.3 (~2)                     | Irreversible        | -                               | -                     | -                               |
| 4-(2-(methacryloyloxy)ethoxy)-4-oxobutanoic acid | 3.10   | -                 | 83.9             | 134.6 (~1.5)                   | Irreversible        | -                               | -                     | -                               |

**ESI 16:** Table of transition temperatures obtained from the DSC heating and cooling runs of various acids mixed with TBIB. Typically the 1st heating and cooling run were used. *No isotropic mixture was obtained, above 206.3 °C degradation seems to start accompanied by phase separation obscuring correct identification of the phases.*
8. Azimuthally integrated XRD diffractograms of mixtures with TBIB

**ESI 17**: X-Ray diffractograms (wide angle) of 3.10 equiv. of dodecanoic, undecanoic acid, tridecanoic acid and tetradecanoic acid mixed with TBIB at 90 °C.

**ESI 18**: X-Ray diffractograms (wide angle) of 3.00 and 3.10 equiv. of hexadecanoic acid mixed with TBIB at 80 °C. No difference in lattice parameters is observed when 3.00 equiv. of acid is used, see thin black line.

**ESI 19**: X-Ray diffractograms (wide angle) of 3.10 equiv. of oleic, linoleic and linolenic acid mixed with TBIB at, respectively, 50 °C, 50 °C and 33 °C. Only for oleic acid (depicted in bold) the Col\textsubscript{hex} phase could be verified by XRD.
ESI 20: X-Ray diffractogram (wide angle) of dimerized linoleic acid (n-DFA, 1.75 equiv.) mixed with TBIB at 33 °C.

ESI 21: X-Ray diffractogram (wide angle) of 4-methyl nonanoic acid (3.10 equiv.) mixed with TBIB at 100 °C.

ESI 22: X-Ray diffractograms (wide angle) of decyl phosphonic acid (3.10 equiv.) mixed with TBIB at two different temperatures. Assigning the correct phase was ambiguous at 180 °C, at 210 °C the phase is believed to be ColN.
ESI 23: X-Ray diffractogram (wide angle) of 4-{2-[(methacryloyloxy)ethoxy]-4-oxobutanoic acid (3.10 equiv.) mixed with TBIB at 95 °C. At q_2 residual TBIB is observed.
9. Transition temperatures and latent heats as a function of equivalents of dodecanoic acid mixed with MeTBIB

**ESI 24:** Clearing temperature and the accompanying latent heat determined from the heating run of MeTBIB mixed with different equiv. dodecanoic acid. Above 3.0 equiv. the transition temperature starts to drop. The latent heat does not show a clear trend.

**ESI 25:** Clearing temperature and the accompanying latent heat determined from the cooling run of MeTBIB mixed with different equiv. dodecanoic acid. Above 3.0 equiv. the transition temperature starts to drop. The latent heat does not show a clear trend.
10. Numerical values of transitions based on DSC for mixtures with MeTBIB

| Acid                     | Equiv. | LC→Isotropic     | Isotropic→LC    |
|--------------------------|--------|------------------|-----------------|
| Dodecanoic acid          | 2.79   | 162.6 (2.77)     | 159.4 (2.43)    |
| “—”                      | 2.83   | 161.9 (3.28)     | 159.3 (3.16)    |
| “—”                      | 2.90   | 162.5 (2.98)     | 160.3 (2.38)    |
| “—”                      | 2.94   | 163.3 (2.97)     | 161.5 (2.36)    |
| “—”                      | 2.98   | 161.0 (3.32)     | 158.8 (3.45)    |
| “—”                      | 2.99   | 162.4 (2.88)     | 161.0 (9.15)    |
| “—”                      | 3.04   | 161.7 (3.07)     | 160.3 (1.88)    |
| “—”                      | 3.10   | 159.6 (3.07)     | 158.0 (2.62)    |
| “—”                      | 3.12   | 158.8 (3.55)     | 157.2 (2.27)    |
| “—”                      | 3.14   | 157.1 (2.79)     | 155.4 (2.64)    |
| “—”                      | 3.19   | 154.6 (2.80)     | 153.5 (2.70)    |
| “—”                      | 3.34   | 150.0 (2.72)     | 147.5 (2.83)    |
| “—”                      | 3.40   | 146.5 (1.82)     | 142.2 (3.52)    |
| “—”                      | 3.49   | 143.2 (1.18)     | 138.6 (3.33)    |
| 4-Dodecylbenzenesulfonic acid | 3.00   | 132.0 (2.26)     | Not detected    |

ESI 26: Table of transition temperatures and latent heats obtained from the DSC heating and cooling runs of dodecanoic acid and 4-dodecylbenzenesulfonic acid mixed with MeTBIB.
11. Azimuthally integrated XRD diffractograms of mixtures with MeTBIB

**ESI 27:** X-Ray diffractogram (wide angle) of dodecanoic acid (2.99 equiv.) mixed with MeTBIB at 105 °C.

**ESI 28:** X-Ray diffractogram (wide angle) of 4-dodecylbenzenesulfonic acid (3.00 equiv.) mixed with MeTBIB at 100 °C.