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

Jody A. M. Lugger and Rint P. Sijbesma*[a]

We report the formation of easily accessible hydrogen-bonded columnar discotic liquid crystals (LCs) based on tris-benzoimidazolyl benzene (**TBIB**) and commercially available fatty acids. By increasing the length of the fatty acid, the temperature range of liquid crystallinity was tuned. Introducing double bonds in octadecanoic acid lowered the crystallization temperature and increased the temperature range of the mesophase. Surprisingly, dimerized linoleic acid also forms an LC phase. When using branched aliphatic acids with the branching point close to the acid moiety, the mesophase was lost, whereas phosphonic acid or benzenesulfonic acid derivatives did have a mesophase, showing that the generality of this approach extends beyond carboxylic acids as the hydrogen-bond donor. Furthermore, a polymerizable LC phase was obtained from mixtures of **TBIB** with a methacrylate-bearing fatty acid, providing an approach for the fabrication of nanoporous polymer films if the methacrylate groups are polymerized. Finally, the higher solubility of methyl-**TBIB** was used to suppress phase separation in stoichiometric mixtures of the template molecule with fatty acids.

1. Introduction

Discotic liquid crystals (DLCs) are currently being investigated for application in various functional materials: for example, semiconductors,[1] nanoporous polymers,[2] displays,[3] and in thermal energy storage.[4] However, the practical applications of DLCs are often limited by lengthy synthetic routes, low solubility, metal impurities, difficult purifications, high clearing points, high melting temperatures, and high viscosity. A strategy to avoid some of these problems is to use a template as the core molecule in combination with hydrogen-bonded peripheral arms in a hydrogen-bonded DLC. Hydrogen-bonded nematic and smectic liquid crystals (LCs) were introduced by Kato et al. and have been investigated thoroughly.[5] Later, hydrogen-bonded DLCs were reported, often with C_3-symmetry based on a heterocyclic template in combination with complementary hydrogen-bonding motifs.[6] The templates are generally easy to prepare, but optimization of the flexible peripheral moieties still requires synthetic effort, limiting application of this concept. A way to circumvent any synthetic effort and to obtain easy accessible DLCs is by combining the hydrogen-bonding capabilities of a simple template with commercially available complementary acids; for example, fatty acids. Such an approach can be used for the fabrication of nanoporous films when combined with a polymerizable acid. After polymerization of the acid and removal of the template, ultimately, a nanoporous membrane may be obtained. Following this design principle, we selected 1,3,5-tris(1 H-benzo[d]imidazol-2-yl)benzene (**TBIB**), a compound known to give LC mixtures with gallic acid derivatives,[7] as the rigid core, and decided to investigate the formation of columnar DLC phases with fatty acids. Fatty acids have previously been used to form nematic and smectic LCs.[8] A supramolecular complex between a DLC oligomer and a simple acid has been reported, but the simple acid did not induce a mesophase.[9] Here, we report C_3-symmetric, hydrogen-bonded columnar DLCs based on a variety of fatty acid homologues in combination with the simple heterocyclic template molecule **TBIB**.

2. Results and Discussion

The synthesis of the template, **TBIB**, was performed as reported by Chandrashekhar et al.[10] These authors purified the product by recrystallization from methanol. However, elemental and ^{1}H NMR analyses showed that subliming **TBIB** significantly improved purity (see the Supporting Information). The increase in purity by sublimation was further confirmed from the clearing point of an LC mixture with dodecanoic acid, which increased by 14 °C upon sublimation (Figure 1).

To explore the tendency of **TBIB** to form mesophases with fatty acids, we initially used the mixture of **TBIB** with 3.00 equivalents of dodecanoic acid. At this stoichiometry,

[a] *J. A. M. Lugger, Prof. Dr. R. P. Sijbesma*
Laboratory of Macromolecular and Organic Chemistry
and the Institute for Complex Molecular Systems
Eindhoven University of Technology
P. O. Box 513, 5600 MB Eindhoven (The Netherlands)
E-mail: r.p.sijbesma@tue.nl

Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/open.201600078.
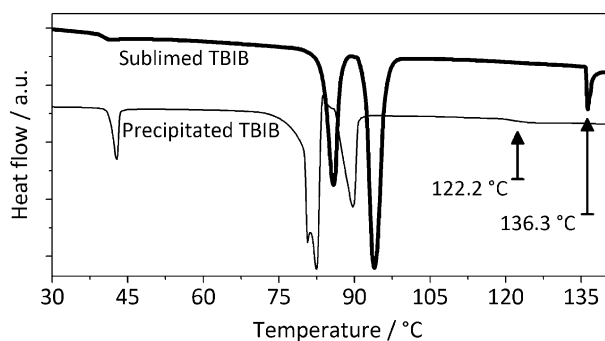
Figure 1. DSC thermograms of two different grades of TBIB mixed with 3.00 equivalents of dodecanoic acid; second heating runs are shown. An increase of 14 °C is observed for the isotropization temperature of the mixture with sublimed TBIB.

Figure 3. Proposed mode of complexation of TBIB with fatty acids, and a list of tested saturated fatty acids. On the right, the methylated analogue MeTBIB is shown.

when using the pure, sublimed **TBIB**, the components were not fully miscible, and solid residue remained present in the isotropic phase. When **TBIB** was mixed with 3.10 equivalents of dodecanoic acid, a residue-free isotropic phase was observed by using polarizing optical microscopy (POM). Similar observations were made for the complex with hexadecanoic acid, and we propose that the poor solubility of **TBIB** in the system requires a small excess of fatty acid to form a homogeneous mixture. In differential scanning calorimetry (DSC) experiments to determine the LC-to-isotropic phase transition temperature at different compositions, the highest phase transition temperatures were observed at 3.10 equivalents of dodecanoic acid (Figure 2). Therefore, in further experiments with all saturated (Figure 3) and unsaturated fatty acids, 3.10 equivalents of acid were used.
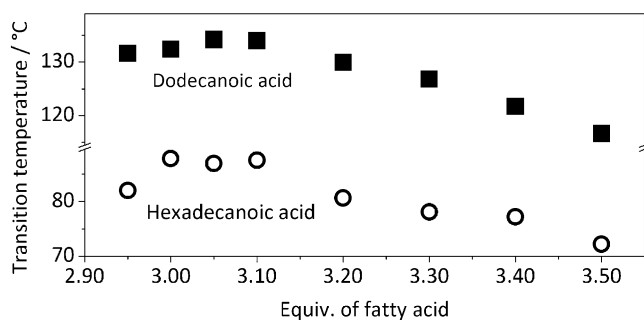
2.94 equivalents of acid, whereas the clearing point of the system reached a maximum for a 1.00:3.00 stoichiometry (see the Supporting Information).

Upon cooling slowly (10 °C min^{-1}) below the isotropization temperature of **TBIB** mixed with 3.10 equivalents of dodecanoic acid (134 °C), a phase with a fan-shaped texture formed (Figure 4), typical for Col$_{hex}$ phases in a random alignment.

Figure 4. Optical microscopy images of the columnar hexagonal LC phase of TBIB mixed with 3.10 equivalents dodecanoic at 130 °C.

Figure 2. Transition temperatures (isotropic-to-LC) observed in the first DSC cooling run for different equivalents of acid added. For both acids shown, dodecanoic and hexadecanoic acid, an optimum at 3.10 equivalents is observed.

Experiments with more soluble derivative 1,3,5-tris(6-methyl-1 H-benzo[d]imidazol-2-yl)benzene (**MeTBIB**) confirmed the hypothesis that low solubility causes the need for an excess of **TBIB** to obtain a single-phase mixture. The 1:3 mixture of **MeTBIB** with dodecanoic acid had a mesophase between 70 and 162 °C, identified as columnar hexagonal (Col$_{hex}$) with powder X-ray diffraction (XRD) and POM. No phase separation was observed with POM in the isotropic phase down to
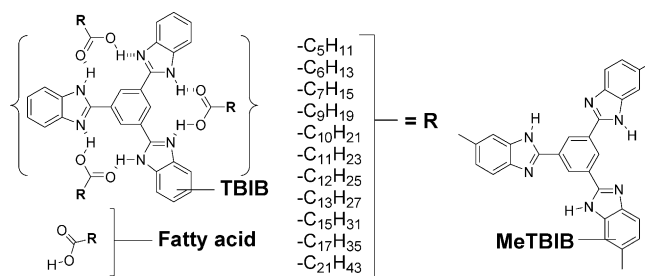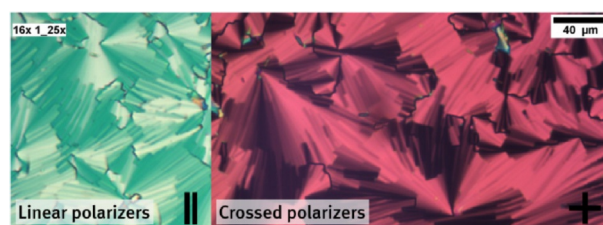
The phase behaviour of the mixture was further investigated by using DSC (Figure 5). In both the heating and cooling runs, three transitions were observed. The first transition of the heating run at 84 °C was determined to be a crystal-to-crystal (K$_1$-to-K$_2$) phase change; at 93 °C, the material enters the LC phase and becomes isotropic at 136 °C. Upon cooling at a rate of 10 °C min^{-1}, the isotropic-to-LC transition showed 1.5 °C super-
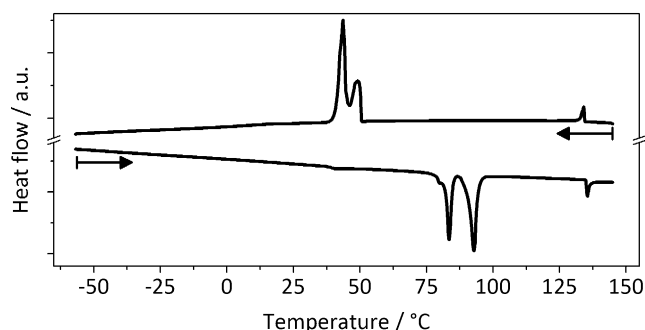

Figure 5. DSC thermograms of TBIB mixed with 3.10 equivalents of dodecanoic acid; second heating and cooling runs are shown. In both the DSC runs, three transitions are observed; the mesophase is found between 94 and 136 °C in the heating curve.

cooling, whereas for the crystallization temperature and the K_2-to-K_1 phase transition supercooling was approximately 40 °C.

In the FTIR spectrum of the LC mixture (Figure 6), the fatty acid C=O stretch vibration shifted to 1691 from 1709 cm^{-1} in the free acid, indicative of the formation of a hydrogen-bonded complex. The band observed at 3263 cm^{-1} in the mixture was assigned to the hydrogen-bonded proton (C=N—H—O) between the benzoimidazolyl moiety and dodecanoic acid.
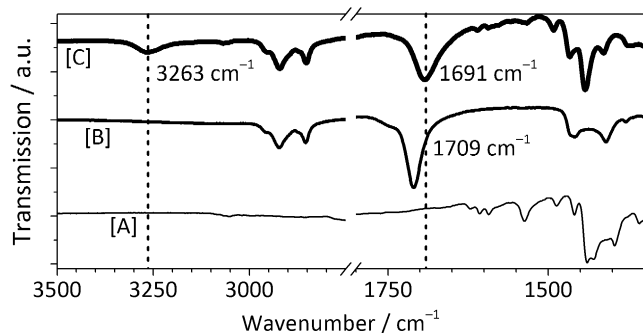

Figure 6. FTIR spectra of TBIB (A), dodecanoic acid (B), and the corresponding mixture with 3.10 equivalents of acid (C) at 110 °C.

The mesophase was further characterized by using XRD (Figure 7). In the diffraction patterns, Bragg peaks were observed at $q_1 = 0.313$ Å^{-1} and $q_2 = 0.544$ Å^{-1}, corresponding to the $d_{(100)}$ and $d_{(110)}$ diffraction planes of a hexagonal lattice ($q_2/q_1 = \sqrt{3}$). An inter-disc distance was observed at $q_4 = 1.855$ Å^{-1}, diffraction plane $d_{(001)}$, which confirms that the observed LC phase is Col$_{hex}$. The broad peak observed at $q_3 = 1.358$ Å^{-1} belongs to the order in the aliphatic tails of the LC.
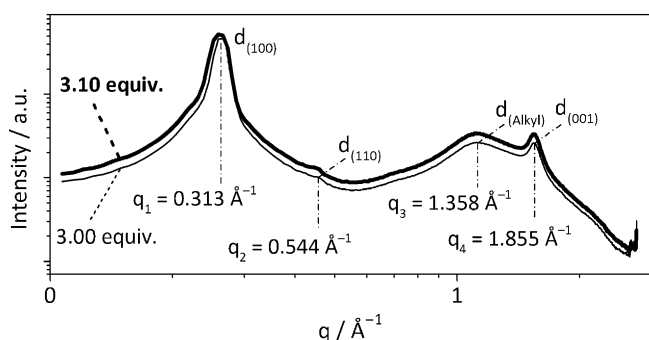

Figure 7. 1D XRD diffraction pattern of the Col$_{hex}$ mesophase at 105 °C for a mixture of TBIB with 3.10 and 3.00 equivalents of dodecanoic acid.

The generality of mesophase formation of these **TBIB**/fatty acid complexes was tested by mixing a range of saturated fatty acid homologues with **TBIB** in a 3.10:1 stoichiometry (Figure 3). Figure 8 shows the phase transition temperatures of saturated fatty acid homologues mixed with **TBIB**. The diagram shows that for shorter acids crystallinity prevails, whereas for longer aliphatic acids the isotropization temperature is lowered; which is in line with earlier observations.[11] The isotropi-
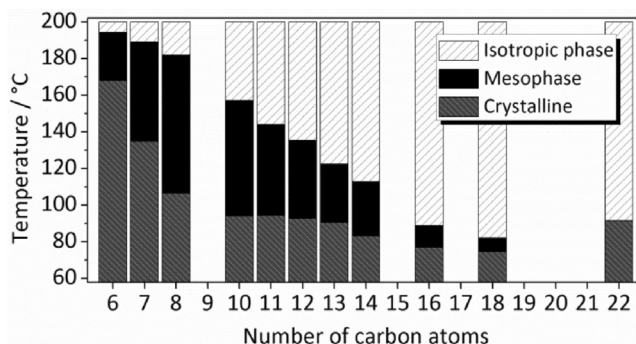

Figure 8. Transition temperatures of TBIB/saturated fatty acid mixtures (3.10 equiv). DSC data from first heating runs were used.

zation temperature seems to be linearly dependent on the fatty acid chain length. The mesophase was determined to be columnar hexagonal for decanoic acid to hexadecanoic acid with POM and XRD (see the Supporting Information). The mesophases of the mixtures with hexanoic and heptanoic acid were inaccessible at atmospheric pressure, owing to the low boiling points of the acids.

By extrapolation of the results shown in Figure 8, one can predict that homologues larger than octadecanoic acid will not have an appreciable mesophase. Hence, the lack of a mesophase in case of docosanoic acid came as no surprise. The phase observed for octadecanoic acid itself deviated from the generally observed LC phase. By using XRD, the phase was determined to be Col$_N$ (see the Supporting Information). In addition to the effects of chain length, the influence of unsaturation of the fatty acid was investigated. Complexes with octadecanoic acid and its unsaturated homologues (9Z)-octadeca-9-enoic acid (oleic acid), (9Z,12Z)-octadeca-9,12-dienoic acid (linoleic acid), and (9Z,12Z,15Z)-octadeca-9,12,15-trienoic acid (linolenic acid), with respectively 1, 2, and 3 non-conjugated cis-double bonds were studied. Figure 9 shows the transition temperatures of the mixtures. The temperature range over which the complexes are LCs increases from 8 °C to 91 °C when the number of double bonds increases from 0 to 3.
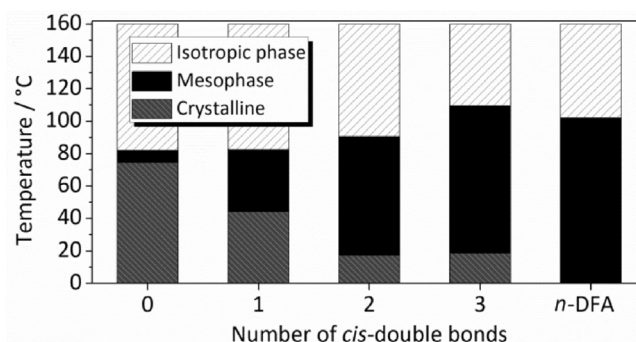
Figure 9. DSC transition temperatures of 1:3.10 mixtures of TBIB with C-18 fatty acids with different degrees of unsaturation. Entry 0: Octadecanoic acid; entry 1: (9Z)-octadeca-9-enoic acid; entry 2: (9Z,12Z)-octadeca-9,12-dienoic acid; entry 3: (9Z,12Z,15Z)-octadeca-9,12,15-trienoic acid. entry 'n-DFA' represents a 2:3.50 mol/mol mixture of TBIB with dimerized linoleic acid. Second heating runs were used to determine transition temperatures.

To further investigate the scope of the LC behavior of the **TBIB**/fatty acid complexes, the thermotropic properties of a mixture of non-hydrogenated dimerized linoleic acid (*n*-DFA) with **TBIB** was investigated. *n*-DFA consists of a mixture of linear, cyclic, and polycyclic unsaturated dimers of linoleic acid.[12] As **TBIB**/*n*-DFA mixtures with 3.10 equivalents of acid functionalities (TBIB:*n*-DFA = 1:1.55) showed phase separation, 1.75 equivalents of *n*-DFA were used. Cooling this mixture at a rate of 0.1 °C min^{-1} gave a texture typical for a Col$_{hex}$ phase (see the Supporting Information). The mixture has a clearing point of 105 °C, similar to linolenic acid, and a glass transition temperature, T_g, around −20 °C, increasing the width of the mesophase compared to the unsaturated straight chain fatty acids by an additional 30 °C. The mesophase was identified as Col$_{hex}$ by using XRD (see the Supporting Information). Surprisingly, besides the $d_{(110)}$, the $d_{(200)}$ was also observed in the XRD diffraction patter, indicating increased short-range order.

We also investigated the **TBIB**/fatty acid system for tolerance to branching in the fatty acid chain by measuring the thermotropic LC behaviour of mixtures with a range of fatty acids with alkyl side chains. The allowed perturbations on the aliphatic chain, and headgroup, were investigated in more detail by mixing the acids, shown in Figure 10, with **TBIB** and testing them for mesogenicity.
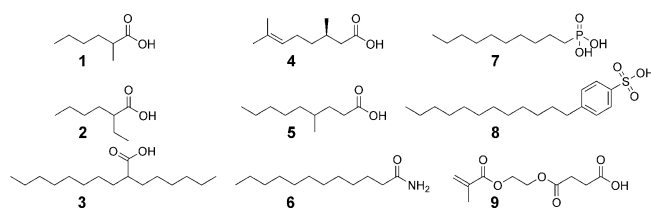

Figure 10. Chemical structures of additional fatty acids tested for mesogenicity.

A mixture with 2-methyl-hexanoic acid lacks a mesophase, perhaps because of the high melting temperature (136 °C). In an attempt to lower the transition temperatures, longer carbon chain lengths were tested. Neither 2-ethyl-hexanoic acid nor 2-hexyl-decanoic acid was mesogenic. Moving the substituent up one carbon atom to the 3-position in the form of 3,7-dimethyl-6-octenoic acid (citronellic acid) did not yield a thermotropic LC mixture either. When 4-methyl-nonanoic acid was used in the mixture with **TBIB**; however, a mesophase was observed with a melting point of 74 °C and an isotropization temperature of 171 °C, similar to the interpolated isotropization temperature for nonanoic acid. The results are summarized in Table 1.

From inspection of space-filling models, it is evident that geometrical constraints prevent accommodation of substituents on the 2- and 3-positions of the fatty acid chain in the plane of the disc-shaped complex. XRD analysis of the mesophase of the **TBIB** complex with 4-methyl-nonanoic showed a $d_{(200)}$ reflection, but the $d_{(110)}$ reflection was missing, which is in contrast to XRD of mixtures with straight chain analogues.

Table 1. Mesogenicity of branched fatty acids and other acids in 3.10:1 mixtures with TBIB and MeTBIB.

Entry	Acid	Phase transition temperatures [°C]
1	*rac*-2-methyl-hexanoic acid	–
2	*rac*-2-ethyl-hexanoic acid	–
3	*rac*-2-hexyl-decanoic acid	–
4	(*R*)-3,7-dimethyloct-6-enoic acid	–
5	*rac*-4-methyl-nonanoic acid	K-73.5-Col$_{hex}$-170.5-I
6	dodecyl-amide	–
7	decyl-phosphonic acid	K-166.7-LC-206.3-Deg.
8	4-dodecylbenzenesulfonic acid[a]	K-100-Col$_N$-132.0-I
9	4-(2-(methacryloyloxy)ethoxy)-4-oxobutanoic acid	K-83.9-Col$_{hex}$-134.6-I

First heating runs were used. [a] This compound was tested with MeTBIB.

However, POM indicated that the mesophase can be identified as Col$_{hex}$ (see the Supporting Information).

When the acid moiety in dodecanoic acid was replaced with an amide group, there was a complete loss of the LC phase. However, decyl-phosphonic acid and 4-dodecylbenzenesulfonic acid (the latter was mixed with MeTBIB) both gave an LC phase. In POM, the phase for both of these mixtures was assigned to be nematic. Unfortunately, the determination of the LC phase using XRD was inconclusive for decyl-phosphonic acid. The mixture with 4-dodecylbenzenesulfonic acid was determined to be columnar nematic (Col$_N$) because of the presence of an inter-disc distance in the XRD profile (see the Supporting Information).[13]

Finally, with an eye towards the potential use of the **TBIB**/fatty acid system for preparing nanoporous polymer materials, the mesogenicity of a polymerizable acid, 4-(2-(methacryloyloxy)ethoxy)-4-oxobutanoic acid, was also tested. A 3.10:1 mixture of 4-(2-(methacryloyloxy)ethoxy)-4-oxobutanoic acid with **TBIB** had a mesophase between 91 and 135 °C, as determined by using POM and DSC. After prolonged exposure to high temperatures, the LC phase was locked-in through thermally initiated cross-linking of the methacrylate moieties. The resulting mesophase was established to be Col$_{hex}$; however, the small excess of acid in the 3.10:1 mixture was not sufficient to completely prevent phase separation, as residual template was observed with both POM and XRD (see the Supporting Information).

3. Conclusions

The results described in this paper chart the scope and limitations of a straightforward method to obtain columnar DLCs by combining commercially available fatty acids with an easily accessible heterocyclic template molecule in hydrogen-bonded, disc-shaped 3:1 complexes. Complexes with a series of fatty acids show LC behavior for chain lengths up to octadecanoic acid. The resulting mixtures required a slight excess of acid to fully dissolve the template when the purity of the heterocycle was increased by introducing a sublimation step. Excess acid is not required when more of the soluble methyl derivative of

tris-benzoimidazolyl benzene was used. Unsaturated homologues of octadecanoic acid considerably increase the phase width from 8 to 91 °C when the number of double bonds increases from 0 to 3. Remarkably, dimerized linoleic acid (a dimerized fatty acid) also forms an LC phase when complexed to this template molecule. In addition to carboxylic acids, sulfonic and phosphonic acids can serve as the hydrogen-bond donor. Branching of the fatty acid close to the acid moiety gave loss of the LC phase, partially limiting the range of useable fatty acids. The wide scope of acids that can form an LC phase with the template molecule means that the **TBIB**/fatty acid combination is easily tailored to specific uses. For example, a polymerizable LC phase was obtained by combining **TBIB** with a methacrylate-bearing fatty acid, providing an approach for the fabrication of nanoporous polymer materials.

Experimental Section

General

The chemicals used were commercial products purchased from either Acros, Sigma–Aldrich, Alfa Aesar, Merck, or Biosolve and used without further purification. Non-hydrogenated dimerized linoleic acid was obtained from CRODA, the Netherlands (trade name Pripol 1012). FTIR spectra were recorded at room temperature on a PerkinElmer Spectrum Two spectrometer equipped with a universal attenuated total reflectance (ATR) sampling accessory. Variable-temperature FTIR spectra were recorded on a Bruker Tensor 27 equipped with a PIKE GladiATR. NMR spectra were recorded at room temperature on a Bruker, FT-NMR spectrometer AVANCE III HD-NanoBay (400 MHz, Bruker UltraSchield magnet, BBFO Probehead, BOSS1 shim assembly) in $[D_6]$DMSO. Chemical shifts are given in ppm with respect to tetramethylsilane (TMS, 0 ppm) as an internal standard. Coupling constants are reported as J values in Hz. Column or flash chromatography was carried out by using silica gel (0.035–0.070 mm, ca. 6 nm pore diameter). POM was performed with a Jeneval microscope equipped with crossed polarizers, a Linkam THMS 600 heating stage, and a Polaroid DMC le CCD camera. DSC measurements were performed in hermetic T-zero aluminium sample pans by using a TA Instruments Q2000–1037 DSC instrument equipped with a RCS90 cooling accessory. Transition temperatures and enthalpies were typically determined from the first cooling and first heating run by using Universal Analysis 2000 software (TA Instruments, USA), with heating and cooling rates of 10 K min^{-1}. XRD profiles were recorded on a Ganesha lab instrument equipped with a Genix-Cu ultra-low divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of 1×10^8 photons s^{-1}. Diffraction patterns were collected using a Pilatus 300 K silicon pixel detector with 487×619 pixels of 172 µm^2 placed at a sample to detector distance of 91 mm. The temperature was controlled with a Linkam HFSX350 heating stage and cooling unit. Azimuthal integration of the diffraction patterns was performed by utilizing the SAXSGUI software. The beam centre and the q-range were calibrated by using silver behenate ($d_{(100)} = 0.1076$ Å^{-1}; 58.39 Å); $d_{(300)}$ was used for the calibration. Measurements were performed on bulk samples sealed in 1.0 mm diameter glass capillaries, 0.01 mm wall thickness (Hilgenberg). The LC mixtures were prepared as follows: the required amount of acid and template were measured separately; typically, 20 mg of total sample was obtained. The acid was analytically transferred to the template by using 500 µL of chloroform. To ensure full dissolution of all components, 100 µL of methanol was added. The solvent

was removed by using a rotary evaporator and the mixture was further dried by using a vacuum pump (<1 mbar). Before testing, each sample was thoroughly mixed.

Synthetic Procedures

Synthesis of 1,3,5-Tris(1H-benzo[d]imidazol-2-yl)benzene (TBIB)

The synthetic procedure was partially adopted from the literature.[14] o-Phenylenediamine (15.439 g, 142.8 mmol, 3 equiv) was condensed with 1,3,5-benzenetricarboxylic acid (10.000 g, 47.6 mmol, 1 equiv) in polyphosphoric acid (70 mL) at 230 °C, overnight. After the reaction the mixture was dissolved in 600 mL of water, the crude product was precipitated by neutralization (pH 8) with sodium bicarbonate. The required purity was obtained after sublimation of the purple precipitate. The sublimation procedure is as follows: a sublimation tube containing concentric rings was charged with 7.0 g of crude product, after which the whole tube was evacuated and the pressure was kept below 1 mbar. The tube was inserted partially into a preheated calcination oven at 400–450 °C. The product was deposited approximately 10 cm from the oven exit on the inside of the concentric rings. Collection of the fine white needles yielded 1.5 g of material, with a 21% overall yield. ^{1}H NMR (400 MHz, $[D_6]$DMSO, 25 °C, TMS): $\delta = 13.38$ (s, 3H; N–H), 9.12 (s, 3H; Ar–H), 7.70 [dd, J(H,H) = 4 Hz; 60 Hz, 6H; Ar–H], 7.28 ppm [d, J(H,H) = 4 Hz, 6H, Ar–H]. ^{13}C NMR (100 MHz, $[D_6]$DMSO, 25 °C, TMS): $\delta = 150.79$, 144.24, 135.79, 132.27, 125.91, 123.45, 122.46, 119.33, 112.22 ppm. Elemental analysis calcd (%) for $C_{27}H_{18}N_6$: C 76.04, H 4.25, N 19.71; found: C 75.88, H 4.06, N 19.42.

Synthesis of 1,3,5-Tris(6-methyl-1H-benzo[d]imidazol-2-yl)-benzene (MeTBIB)

The synthetic procedure was partially adopted from the literature.[14] Polyphosphoric acid (150 g), 4-methylbenzene-1,2-diamine (17.441 g, 142.76 mmol, 3 equiv), and trimesic acid (10.000 g, 47.59 mmol, 1 equiv) were added to a 250 mL round-bottom flask. The two solids were ground together before being added to the flask. The flask was sealed by using a bubble condenser containing mineral oil and heated to 150 °C overnight while stirring. The temperature was further increased to 180 °C for an additional 48 h. After the reaction, the black mixture was poured into water (0.8 L) and the crude product was precipitated by neutralization (pH 8) with sodium bicarbonate. The solids were collected by using a Buchner filter and dried by lyophilization. The resulting purple powder was further purified by using column chromatography (SiO$_2$ 2:1, MeOH, $R_f = 1$, solid loading); removal of the solvent gave a dark solid (58%). The resulting solids were sublimated (see previous method) at 375 °C, using dynamic vacuum (<1 mbar), yielding 5.5 g of white needles (25% overall yield). The compound was found to be a mixture of prototropic tautomers. ^{1}H NMR (400 MHz, $[D_6]$DMSO, 25 °C, TMS, major tautomer): $\delta = 13.18$ (s, 3H; N–H), 9.04 (s, 3H; Ar–H), 7.63 (d, J(H,H) = 8 Hz, 3H; Ar–H), 7.39 (s, 3H; Ar–H), 7.08 (d, J(H,H) = 8 Hz, 3H; Ar–H), 2.48 (s, 9H; –CH$_3$). (minor tautomer): $\delta = 13.22$ (s, 3H; N–H), 9.04 (s, 3H; Ar–H), 7.54 (s, 3H; Ar–H), 7.48 (d, J(H,H) = 8 Hz, 3H; Ar–H), 7.12 (d, J(H,H) = 8 Hz, 3H, Ar–H), 2.47 ppm (s, 9H; –CH$_3$). ^{13}C NMR (100 MHz, $[D_6]$DMSO, 25 °C, TMS, both tautomers): $\delta = 150.73$, 150.35, 144.62, 142.40, 136.05, 133.82, 132.80, 132.33, 131.40, 125.53, 125.47, 125.41, 124.89, 124.06, 119.06, 118.96, 111.85, 111.71, 21.89, 21.83 ppm. Elemental analysis calcd (%) for $C_{30}H_{24}N_6$: C 76.90, H 5.16, N 17.94; found: C 76.50, H 5.23, N 17.90.

Acknowledgements

[1] T. Wöhrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum, J. Litterscheidt, J. C. Haenle, P. Staffeld, A. Baro, F. Giesselmann, S. Laschat, *Chem. Rev.* **2016**, *116*, 1139–1241.

[2] a) A. P. H. J. Schenning, Y. C. Gonzalez-Lemus, I. K. Shishmanova, D. J. Broer, *Liq. Cryst.* **2011**, *38*, 1627–1639; b) G. M. Bögels, J. A. M. Lugger, O. J. G. M. Goor, R. P. Sijbesma, *Adv. Funct. Mater.* **2016**, DOI: 10.1002/adfm.201603408.

[3] H. K. Bisoyi, S. Kumar, *Chem. Soc. Rev.* **2010**, *39*, 264–285.

[4] R. Bayón, E. Rojas, *Int. J. Energy Res.* **2013**, *37*, 1737–1742.

[5] a) T. Kato, J. M. J. Frechet, *J. Am. Chem. Soc.* **1989**, *111*, 8533–8534; b) C. M. Paleos, D. Tsiourvas, *Liq. Cryst.* **2001**, *28*, 1127–1161.

[6] a) S. Castelar, J. Barberá, M. Marcos, P. Romero, J.-L. Serrano, A. Golemme, R. Termine, *J. Mater. Chem. C* **2013**, *1*, 7321–7332; b) F. Vera, J. L. Serrano, M. P. D. Santo, R. Barberi, M. B. Ros, T. Sierra, *J. Mater. Chem.* **2012**, *22*, 18025–18032; c) J. R. Avilés Moreno, J. J. López González, F. Partal Ureña, F. Vera, M. B. Ros, T. Sierra, *J. Phys. Chem. B* **2012**, *116*, 5090–5096; d) A. A. Vieira, H. Gallardo, J. Barberá, P. Romero, J. L. Serrano, T. Sierra, *J. Mater. Chem.* **2011**, *21*, 5916–5922; e) F. Vera, J. Barberá, P. Romero, J. L. Serrano, M. B. Ros, T. Sierra, *Angew. Chem. Int. Ed.* **2010**, *49*, 4910–4914; *Angew. Chem.* **2010**, *122*, 5030–5034; f) F. Vera, R. M. Tejedor, P. Romero, J. Barberá, M. B. Ros, J. L. Serrano, T. Sierra, *Angew. Chem. Int. Ed.* **2007**, *46*, 1873–1877; *Angew. Chem.* **2007**, *119*, 1905–1909; g) L. Álvarez, J. Barberá, L. Puig, P. Romero, J. L. Serrano, T. Sierra, *J. Mater. Chem.* **2006**, *16*, 3768–3773; h) J. Barberá, L. Puig, P. Romero, J. L. Serrano, T. Sierra, *J. Am. Chem. Soc.* **2006**, *128*, 4487–4492; i) A. Kraft, A. Reichert, R. Kleppinger, *Chem. Commun.* **2000**, 1015–1016; j) A. Kraft, F. Osterod, R. Fröhlich, *J. Org. Chem.* **1999**, *64*, 6425–6433; k) H.-K. Lee, H. Lee, Y. H. Ko, Y. J. Chang, N.-K. Oh, W.-C. Zin, K. Kim, *Angew. Chem. Int. Ed.* **2001**, *40*, 2669–2671; *Angew. Chem.* **2001**, *113*, 2741–2743; l) J. H. Lee, S. J. Lee, J. Y. Jho, *Phase Transitions* **2014**, *87*, 656–665; m) J. H. Lee, *Liq. Cryst.* **2014**, *41*, 738–746; n) S. J. Lee, J. Lee, S. W. Lee, J. H. Lee, J. Y. Jho, *J. Ind. Eng. Chem.* **2012**, *18*, 767–774; o) M.-H. Ryu, J.-W. Choi, H.-J. Kim, N. Park, B.-K. Cho, *Angew. Chem. Int. Ed.* **2011**, *50*, 5737–5740; *Angew. Chem.* **2011**, *123*, 5855–5858; p) M. Lehmann, P. Maier, *Angew. Chem. Int. Ed.* **2015**, *54*, 9710–9714; *Angew. Chem.* **2015**, *127*, 9846–9850; q) D. Goldmann, D. Janietz, C. Schmidt, J. H. Wendorff, *J. Mater. Chem.* **2004**, *14*, 1521–1525.

[7] J.-F. Xiong, S.-H. Luo, J.-P. Huo, J.-Y. Liu, S.-X. Chen, Z.-Y. Wang, *J. Org. Chem.* **2014**, *79*, 8366–8373.

[8] B. Gundogan, K. Binnemans, *Liq. Cryst.* **2000**, *27*, 851–858.

[9] K.-Q. Zhao, X.-Y. Bai, B. Xiao, Y. Gao, P. Hu, B.-Q. Wang, Q.-D. Zeng, C. Wang, B. Heinrich, B. Donnio, *J. Mater. Chem. C* **2015**, *3*, 11735–11746.

[10] N. Chandrashekhar, B. Thomas, V. Gayathri, K. V. Ramanathan, N. M. N. Gowda, *Magn. Reson. Chem.* **2008**, *46*, 769–774.

[11] W. Acree Jr, J. S. Chickos, *J. Phys. Chem. Ref. Data* **2006**, *35*, 1051–1330.

[12] T. E. Breuer, *Kirk-Othmer Encycl. Chem. Technol.*, John Wiley & Sons, Inc., New York, NY, **2000**.

[13] P. H. J. Kouwer, W. F. Jager, W. J. Mijs, S. J. Picken, *Macromolecules* **2000**, *33*, 4336–4342.

[14] J.-F. Xiong, J.-X. Li, G.-Z. Mo, J.-P. Huo, J.-Y. Liu, X.-Y. Chen, Z.-Y. Wang, *J. Org. Chem.* **2014**, *79*, 11619–11630.