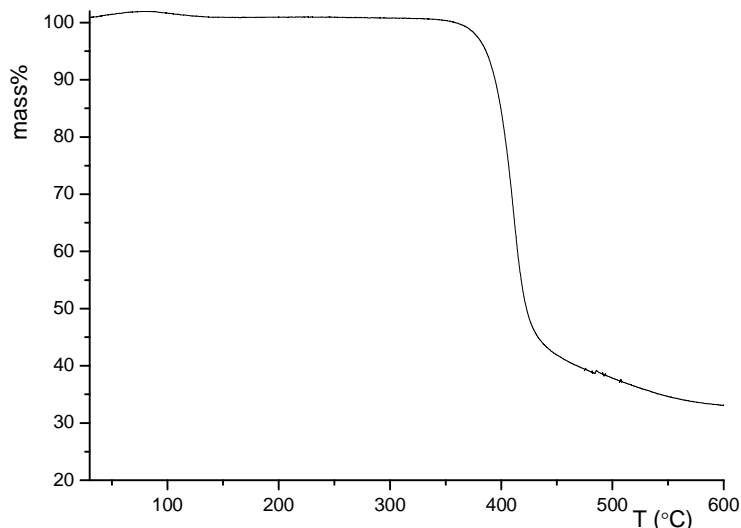


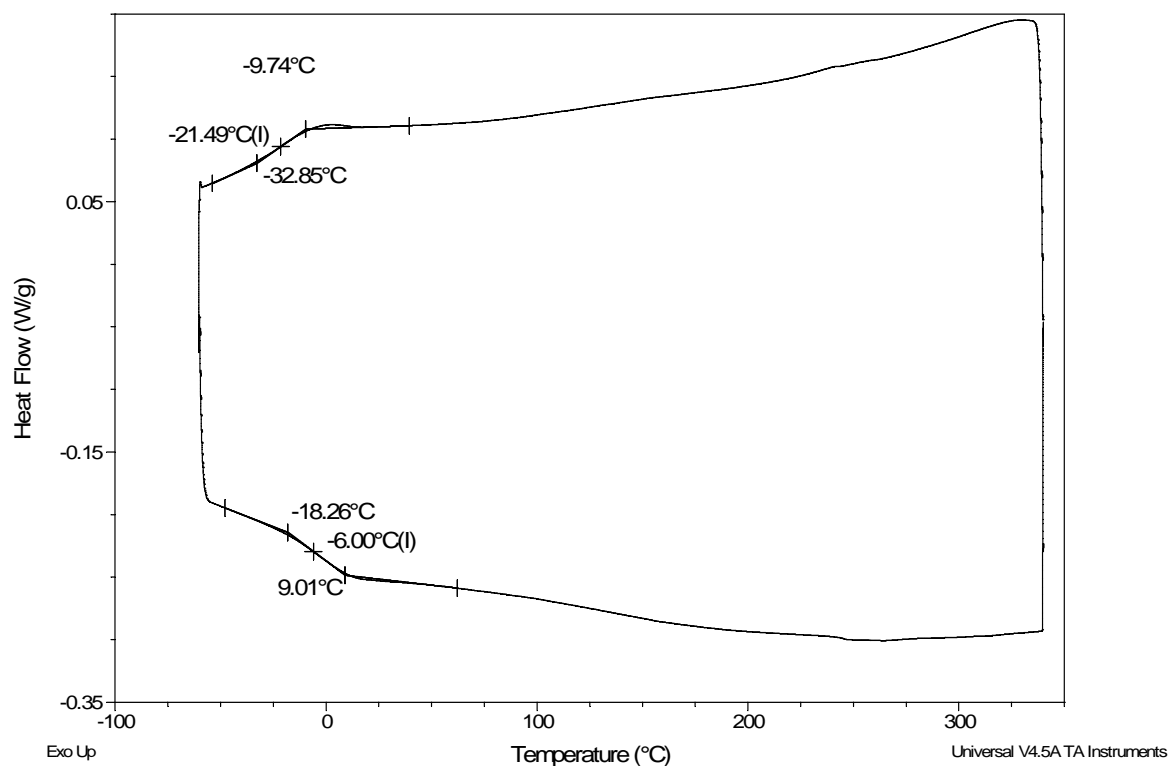
## Helical self-assembly and co-assembly of fluorinated, preorganized discotics

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### Supporting Information



**Figure S1.** Thermal gravimetric analysis of discotic **1** under nitrogen. Heating rate: 10 °C/Min.



**Figure S2.** DSC run of discotic **1**. Shown are the first cooling run and the second heating run; the heating run is shown at bottom. Cooling/heating rates are 10 °C/min.

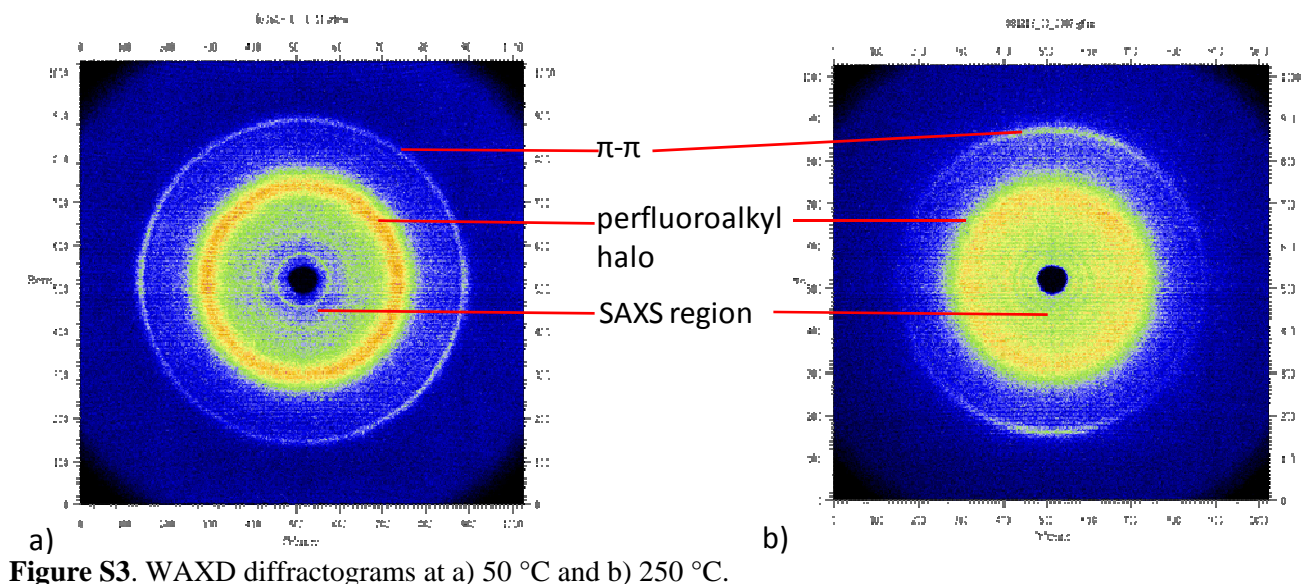


Figure S3. WAXD diffractograms at a) 50 °C and b) 250 °C.

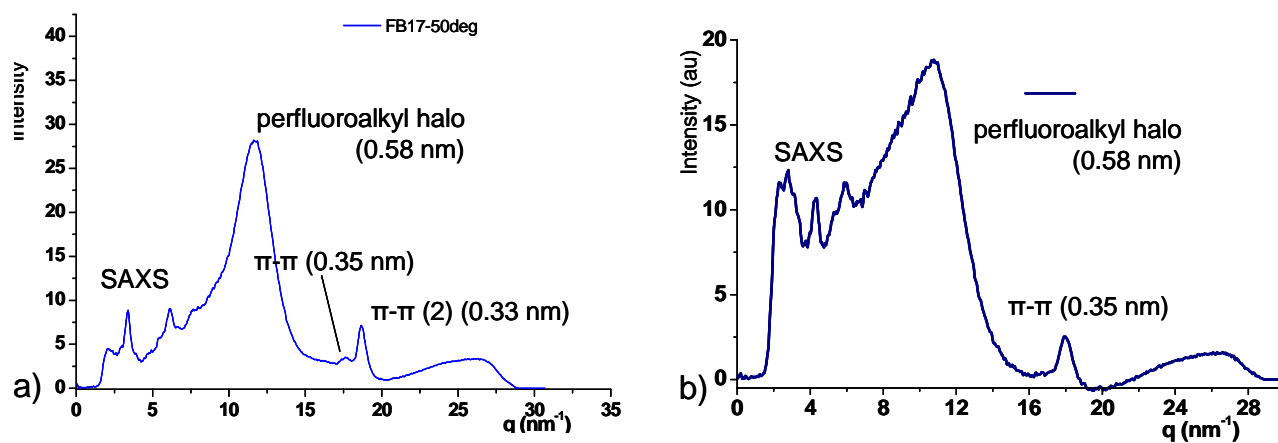


Figure S4. Integrated WAXD profiles at a) 50 °C and b) 250 °C.

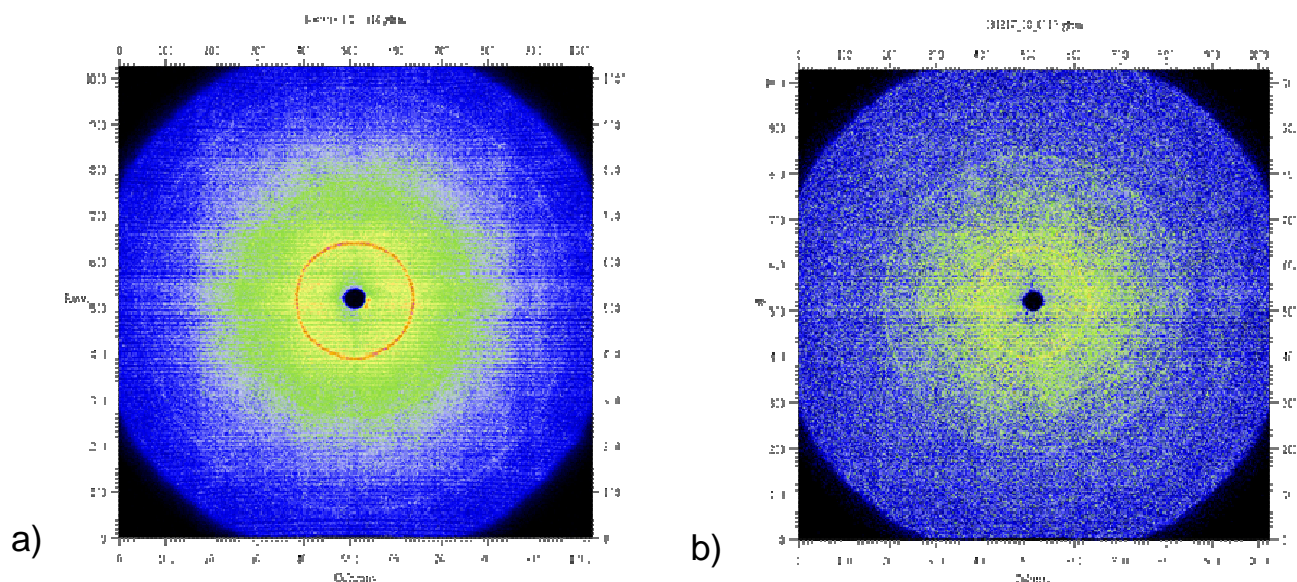


Figure S5. SAXD diffractograms at a) 50 °C and b) 250 °C.

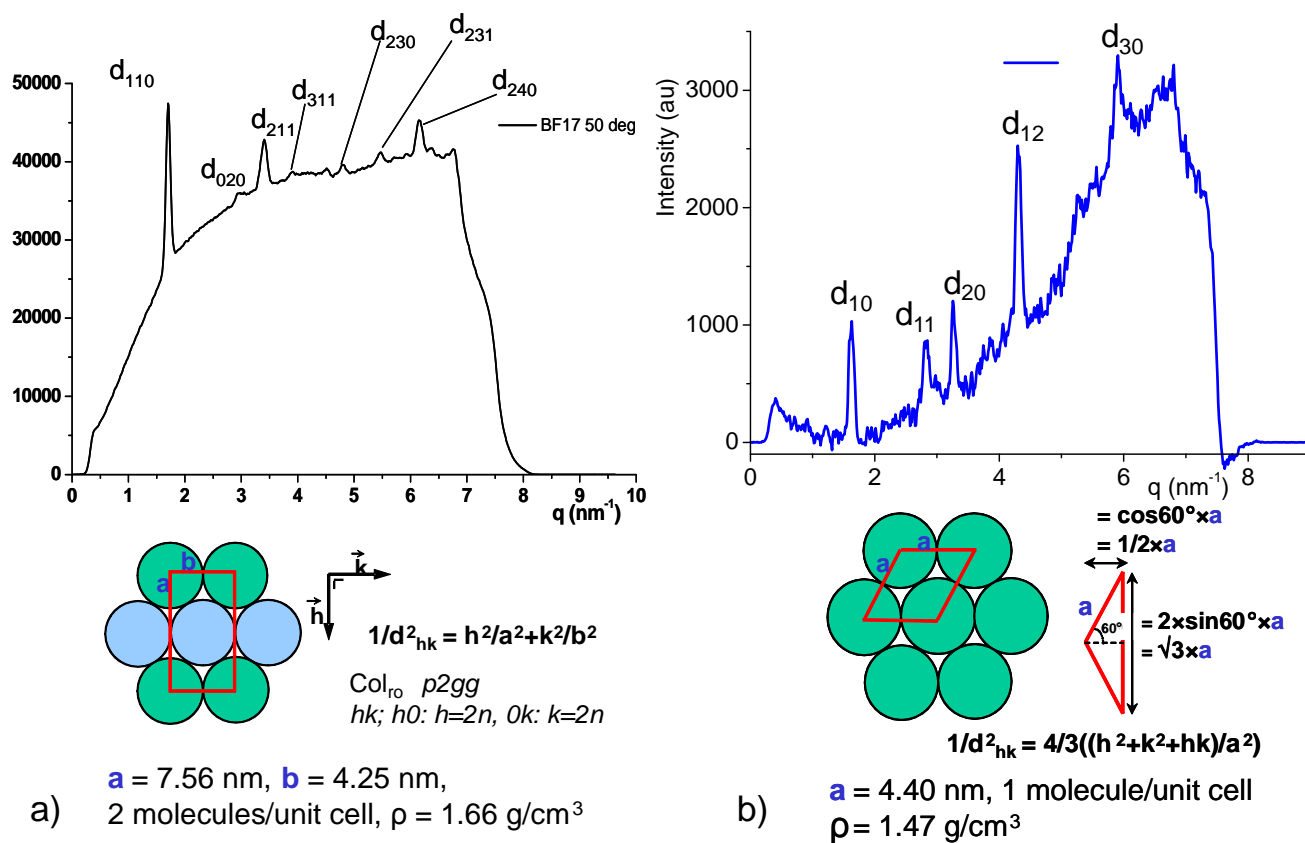


Figure S6. Integrated SAXD profiles at a) 50 °C and b) 250 °C. Also the lattice parameters are shown.

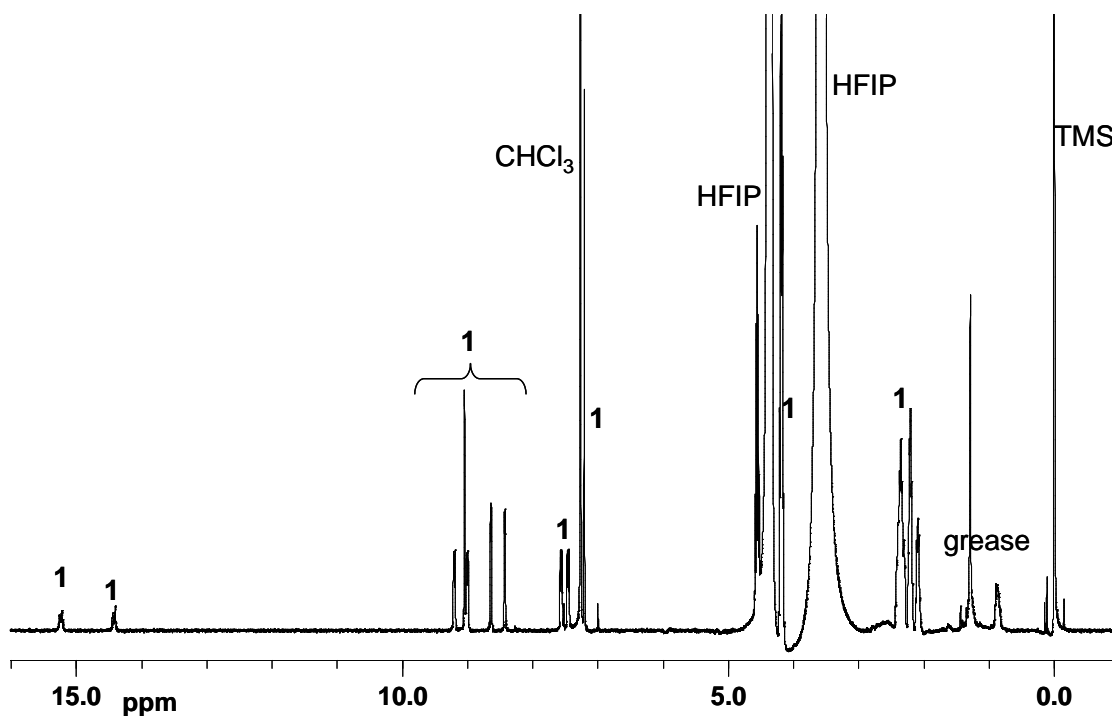
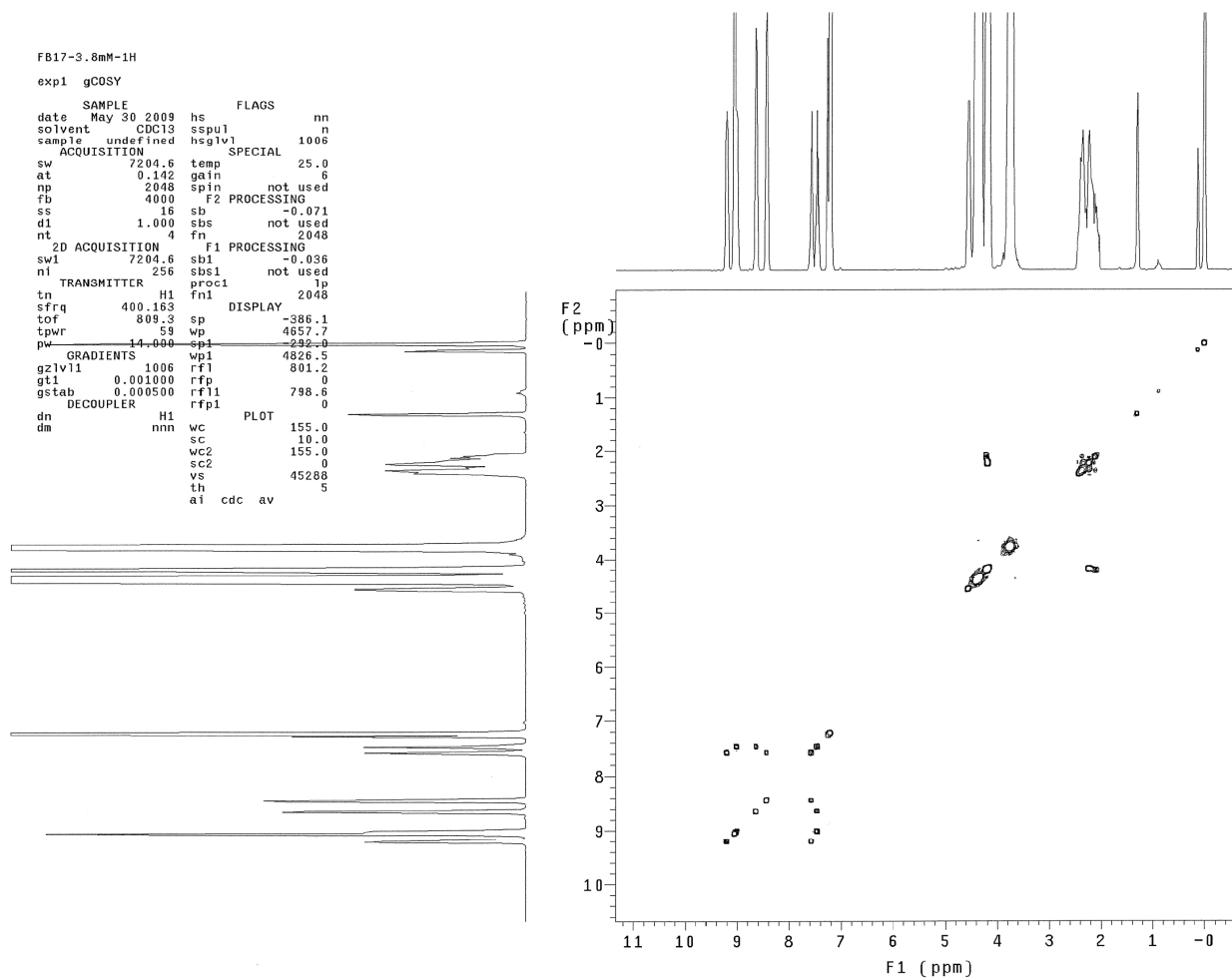
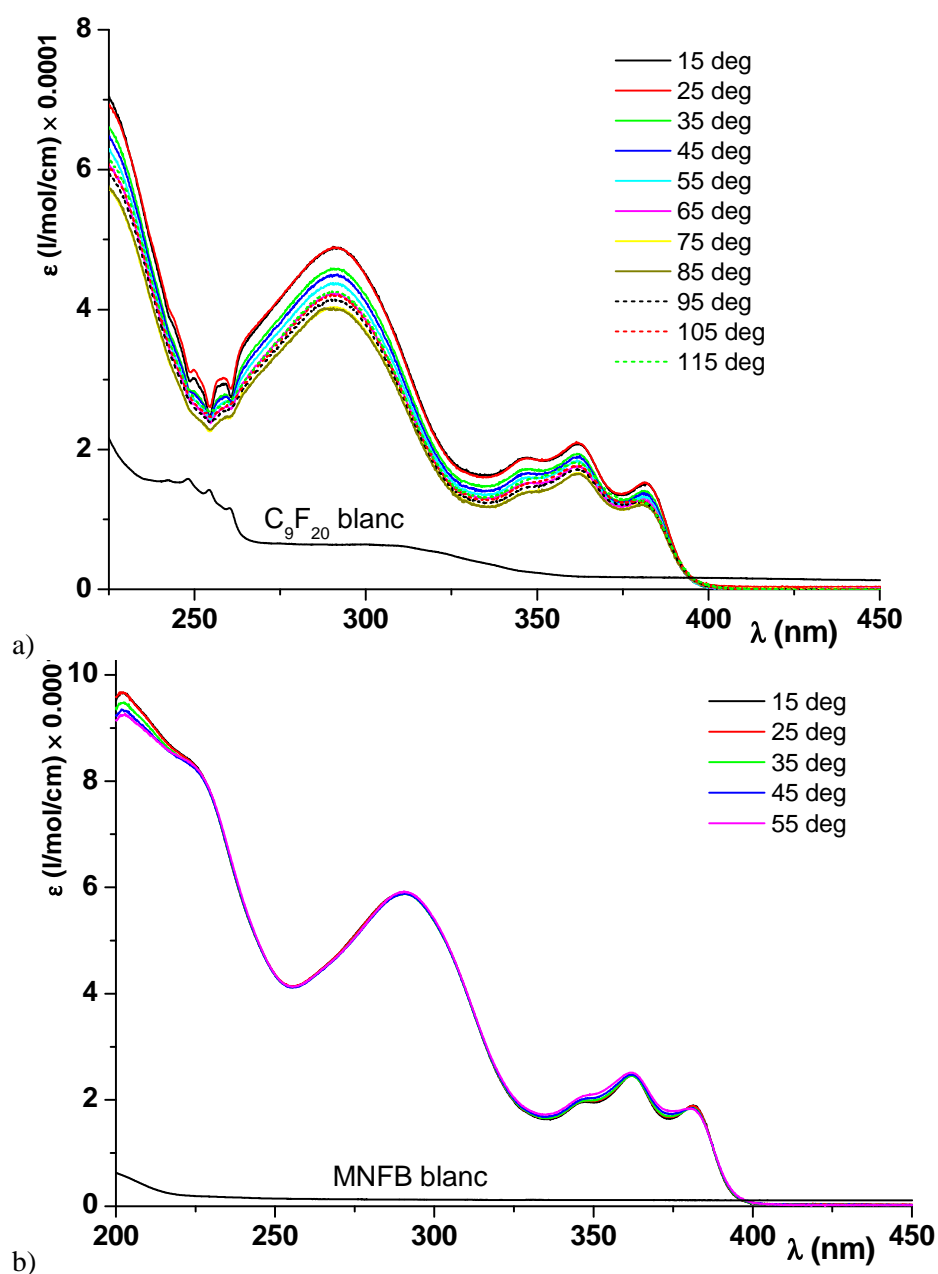


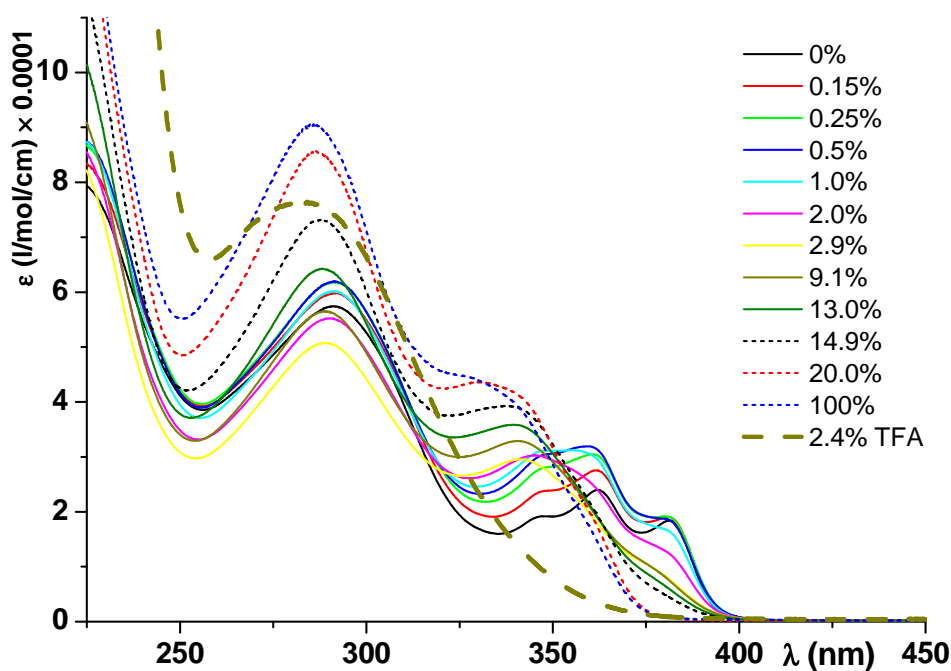
Figure S7. Full <sup>1</sup>H-NMR spectrum of discotic **1** in HFIP/HFIP-D<sub>2</sub>/CDCl<sub>3</sub> (20 vol% HFIP/HFIP-D<sub>2</sub> (1:1)-CDCl<sub>3</sub>, 3.8 mM). Indication **1** refers to peaks belonging to the product. Peak assignment is given in the experimental section.



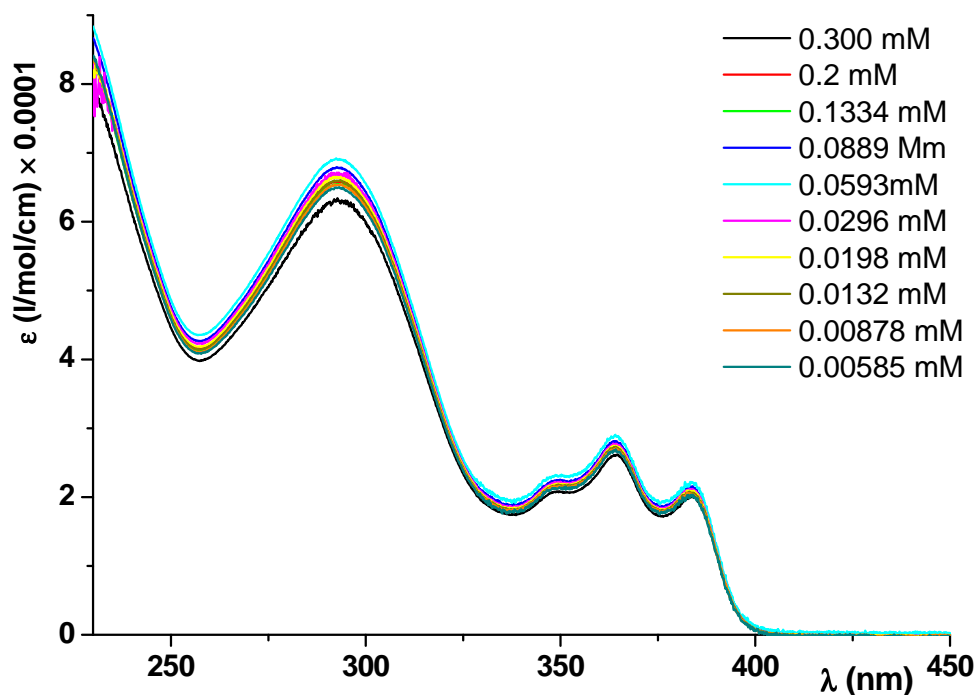
**Figure S8.** a) gCOSY spectrum of discotic **1** in HFIP/HFIP-D<sub>2</sub>/CDCl<sub>3</sub> (20 vol% HFIP/HFIP-D<sub>2</sub> (1:1)-CDCl<sub>3</sub>, 3.8 mM).



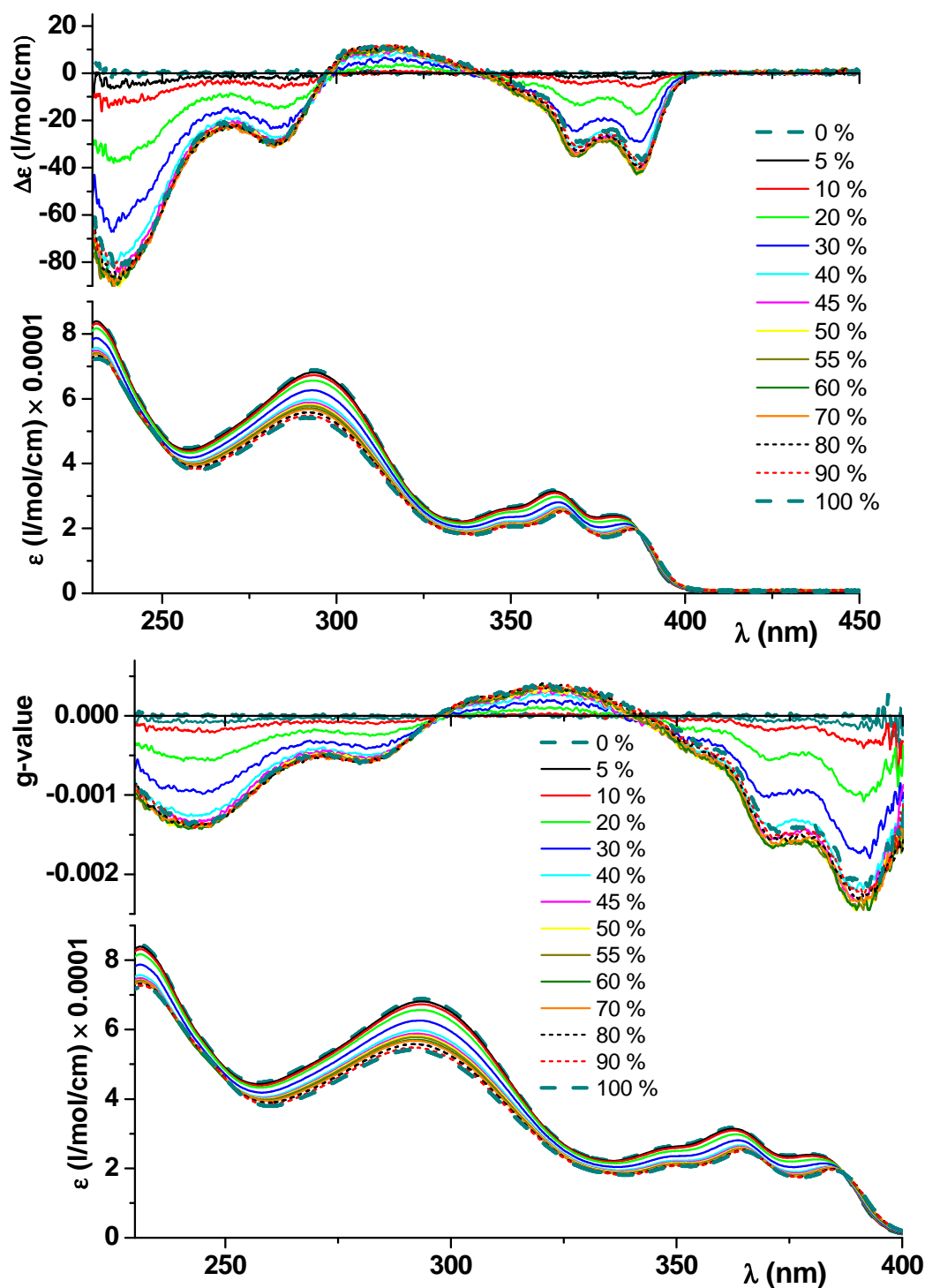
b) **Figure S9.** a) Unnormalized UV/Vis absorption spectra of discotic **1** in a)  $C_9F_{20}$  (5.5  $\mu$ M), b) MNFB ( $CH_3OC_4F_9$ ) (5.7  $\mu$ M) at several temperatures. Also the absorption of the used solvents is shown.



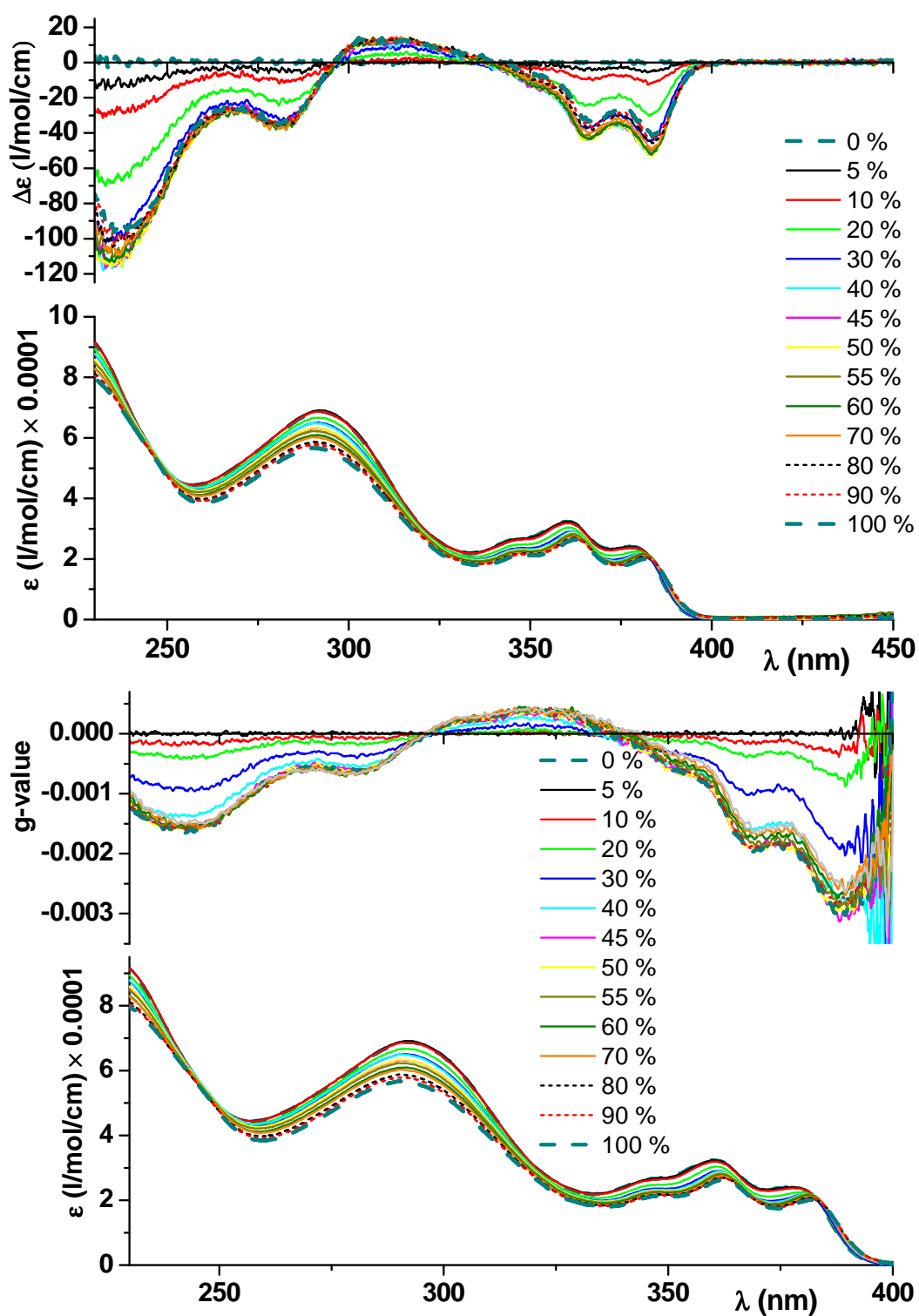
**Figure S10.** Spectral data upon progressive addition of a 17  $\mu\text{M}$  solution of disc **1** in HFIP to a 17  $\mu\text{M}$  solution of disc **1** in MNFB at room temperature, from which Figure 5b is obtained. Percentages correspond to volume-% of the 17  $\mu\text{M}$  solution of disc **1** in HFIP.



**Figure S11.** Concentration dependent UV/Vis absorption spectra of disc **2** in the presence of 10 mol% disc **1** in F1-10 (1:10 v:v mixture of methoxynonafluorobutane and 1,1,2-trichloro-1,2,2-trifluoroethane).

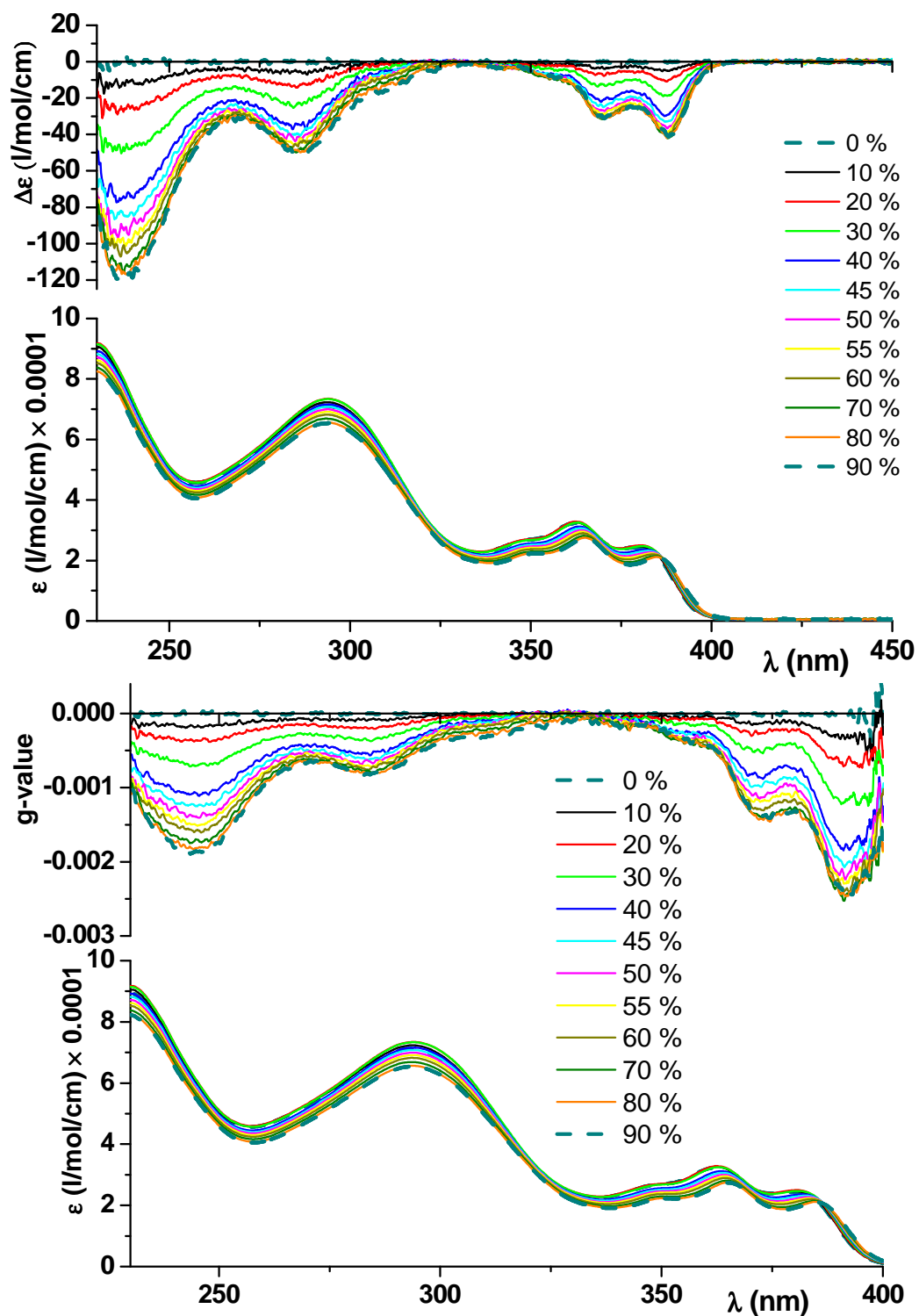


**Figure S12.** Full CD ( $\Delta\epsilon$  and g-value) and UV/Vis absorption spectra corresponding to Figure 8a. Mixing experiments of equimolar solutions of discs **1** and **3**. Concentration = 15  $\mu$ M in **F1-10**. Percentages correspond to volume-% of 15  $\mu$ M chiral disc solution in **F1-10** added.

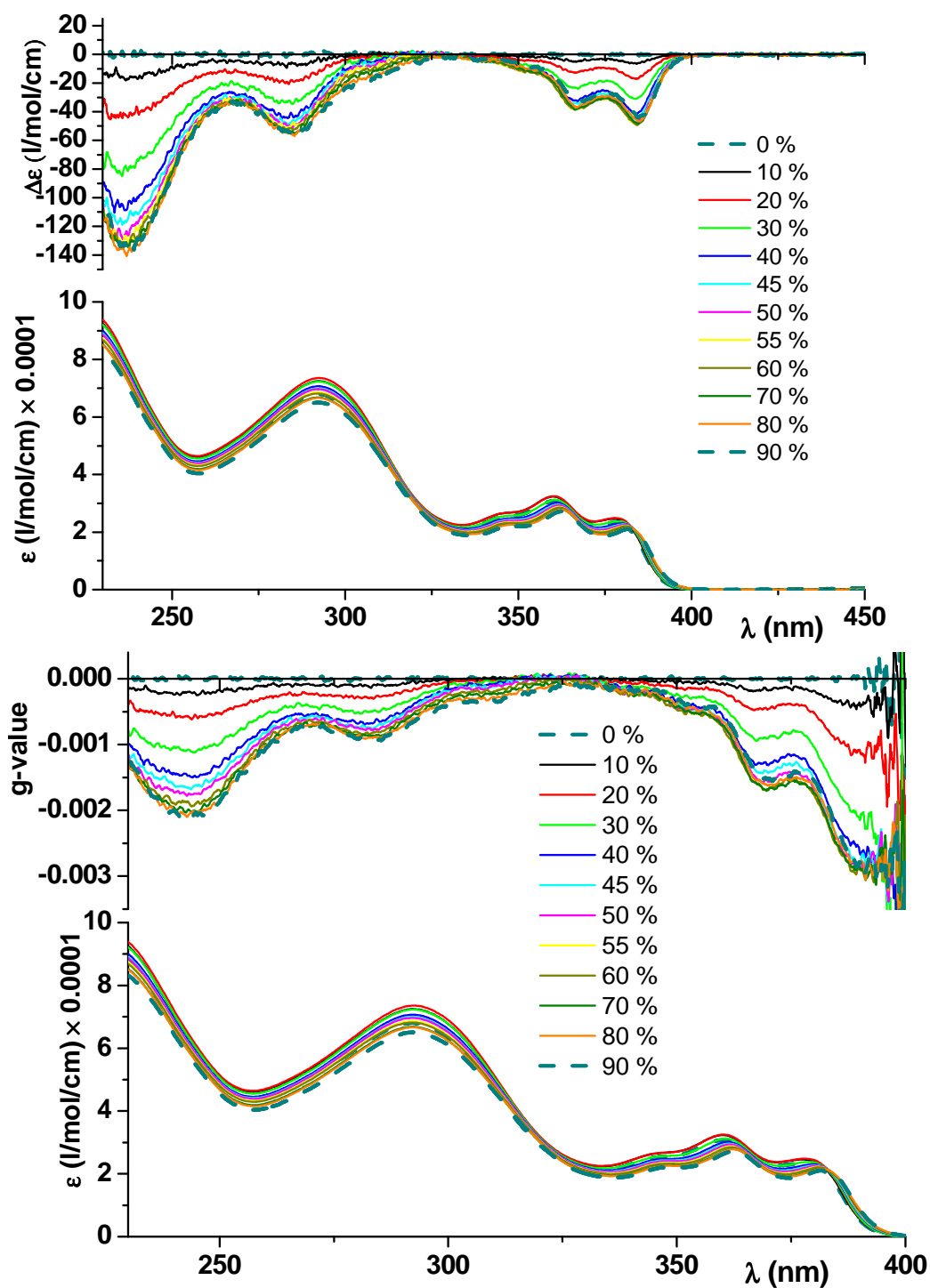


**Figure S13.** Full CD ( $\Delta\epsilon$  and g-values) and UV/Vis absorption spectra corresponding to Figure 8b. Mixing experiments of equimolar solutions of discs **1** and **3**. Concentration = 100  $\mu\text{M}$  in **F1-10**. Percentages correspond to volume-% of 15  $\mu\text{M}$  chiral disc solution in **F1-10** added.





**Figure S14.** Full CD ( $\Delta\epsilon$  and g-values) and UV/Vis absorption spectra corresponding to Figure 9a. Mixing experiments of a solution of disc 1 and a solution of disc 2 containing 10 mol% disc 1. Concentration = 15  $\mu\text{M}$  in F1-10. Percentages correspond to volume-% of 15  $\mu\text{M}$  chiral disc solution in F1-10 added.



**Figure S15.** Full CD ( $\Delta\epsilon$  and g-values) and UV/Vis absorption spectra corresponding to Figure 9b. Mixing experiments of a solution of disc **1** and a solution of disc **2** containing 10 mol% disc **1**. Concentration = 150  $\mu$ M in F1-10. Percentages correspond to volume-% of 15  $\mu$ M chiral disc solution in F1-10 added.

## Experimental section

The synthesis of 3'-*tertiary*-butoxycarbonylamino-2,2'-bipyridine-3-amine (**9**)<sup>[1]</sup> has been described previously. All solvents were of AR quality if not stated otherwise and were purchased from Biosolve (www.biosolve.nl). Trimesyl chloride, tetrabutylammonium bromide, potassium carbonate, methyl isobutyl ketone, oxalyl chloride, trifluoroacetic acid and magnesium sulphate were purchased from Acros (www.acros.be). Triethylamine and 1-iodo,1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecane (**5**) were purchased from Fluka (www.aldrich.com). Sodium carbonate and sodium hydroxide were purchased from Merck (www.merck.nl). Methoxynonafluorobutane (MNFB), hexafluoroisopropanol ( $\geq 99.8\%$ , spectroscopic grade) and 1,1,2-trichloro-1,2,2-trifluoroethane (Freon) (HPLC grade) were purchased from Aldrich (www.aldrich.com). Hexafluoroisopropanol (97 %, used for column chromatography) was purchased from ABCR (www.ABCR.de). Perfluorononane was purchased from Fluorochem (www.fluorochem.co.uk). Deuterated solvents were purchased from Cambridge Isotope Laboratories (www.isotope.com) and were dried over molsieves. Methoxynonafluorobutane (MNFB) was dried over 4 Å molsieves before use. Potassium carbonate was powdered and dried in a vacuum-oven before use. Dichloromethane was distilled over Merck P<sub>2</sub>O<sub>5</sub>. Water was demineralised before use. Triethylamine was stored over KOH. Column chromatography was carried out using Merck 60 Å pore size silica gel (particle size: 63-200 µm) or flash silica gel (particle size: 40-63 µm), TLC was performed on Merck Kieselgel F-254 precoated silica gel 60 Å plates with detection by UV light at 254 or 365 nm. Spectroscopy and chromatography were performed at room temperature unless stated otherwise. Analytical GPC was performed using a Shimadzu system equipped with a Shimadzu LC-10ADvp pump, 2 × PL gel 3 µm 100 Å columns in series and a Shimadzu SPD-M10Avp PDA detection system with detection at 290 nm and 350 nm; chloroform was used as the eluent with a flow of 1 mL/min. Manual injection was performed and the injection volume amounted to 20 µL. Melting points were determined using a Büchi Melting Point B-540 device and measurements were performed in duplo. <sup>1</sup>H-NMR and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury Vx 400 MHz (100 for <sup>13</sup>C, 375 MHz for <sup>19</sup>F) a Varian 400-MR 400 MHz (100 for <sup>13</sup>C, 375 MHz for <sup>19</sup>F), a Varian Gemini 300 MHz (75 MHz for <sup>13</sup>C) or a Varian Mercury Plus 200 MHz (50 MHz for <sup>13</sup>C, 188 MHz for <sup>19</sup>F) NMR spectrometer. <sup>1</sup>H Chemical shifts were determined using tetramethylsilane as internal standard (0 ppm), and are given in ppm. <sup>13</sup>C chemical shifts were determined using the deuterated solvent CDCl<sub>3</sub> (77.16 ppm) or tetramethylsilane (0 ppm) as internal standards. <sup>19</sup>F chemical shifts were calculated by the Varian software using CCl<sub>3</sub>F as standard. gCOSY 2D experiments were performed in CDCl<sub>3</sub> on a Varian Mercury 400 MHz spectrometer using standard Varian parameters for CDCl<sub>3</sub>. Infrared spectra were recorded in the solid state or as a liquid film on a Perkin Elmer Spectrum One 1600 FT-IR spectrometer, equipped with a Perkin Elmer Universal ATR Sampler Accessory. Wavelengths are given in cm<sup>-1</sup>. UV/Vis spectra were recorded on a Perkin Elmer Lambda 40 UV/Vis spectrometer equipped with a Perkin Elmer PTP-1 Peltier temperature control system and fluorescence spectra were measured on a Perkin Elmer LS50B luminescence spectrometer equipped with a Perkin Elmer PTP-1 Peltier temperature control system. Quartz cuvettes (1 cm or 1 mm) were used for the measurements, wavelengths are given in nm and absorptions (extinction coefficients, ε) in l/mol/cm. For temperature dependent measurements, a screw-cap sealed quartz cuvette was used. CD spectra were recorded on a Jasco J-815 spectropolarimeter equipped with a Jasco PTC-413S/15 Peltier type temperature control system. The CD effect is given in Δε (L/mol/cm) and is calculated by: Δε = (CD effect)/(c×l×32980), where CD effect = measured CD effect in mdeg, c = disc concentration in mol/L and l = cuvette path length in cm. Solutions are made by addition of the appropriate amount of solvent to the weighted sample and subsequent dissolution by gentle heating and sonication. Mixtures are made from two solutions followed by a heating and cooling step (annealing). During chiral optical measurements with CD spectroscopy especially the concentrated solutions were checked for the occurrence of linear dichroism, since this may influence the apparent CD signal.<sup>[2]</sup> Spectroscopic measurements were done at room

temperature when no exact temperature is given. Matrix assisted laser desorption/ionisation mass spectra were measured on a Perseptive Biosystems Voyager-DE PRO spectrometer with a Biospectrometry workstation,  $\alpha$ -Cyano-4-hydroxycinnamic acid (CHCA) or 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malononitrile (DCTB) were used as matrix material. *M/z* values are given in g/mol. Elemental analysis was performed using a Perkin Elmer 2400 series II CHNS/O analyser and the elemental content is given in weight percentages.

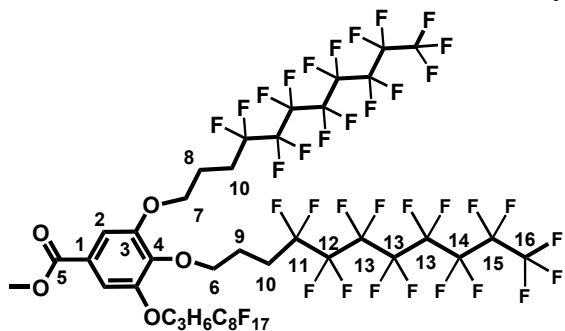
Thermal gravimetric analysis (TGA) was carried out on a Perkin Elmer Pyris 6 Thermogravimetric Analyser. Heating was performed from 30 °C till 600 °C with a rate of 10 °C per minute under a nitrogen or oxygen atmosphere. Polarized optical microscope images were made on a Carl-Zeiss Jenaval polarization microscope (crossed polarizers) equipped with a Linkam THMS 600 heating device and a Polaroid digital camera model PDMC-2. Measurements were performed under a nitrogen atmosphere to prevent thermal degradation. DSC analysis was performed on a TA Q2000 instrument under a nitrogen atmosphere.

The samples for wide angle X-ray diffraction (WAXD) and small angle X-ray diffraction (SAXD) were prepared in 0.7 mm Lindemann glass capillaries. Shear alignment was performed (if possible) by rubbing the sample inside the capillary at 250 °C inside a melting point apparatus (A Büchi Melting Point B-540 device). At this temperature, the mesophase is fluid enough to be processed by shearing without destroying the fragile capillary. The samples were analyzed on a Bruker-Nonius D8-Discover X-ray diffractometer with a 0.154 nm Cu radiation source, equipped with a home-build sample oven. (TU Delft). The scattering data were recorded on a 2D detector (1024×1024) and the sample-to-detector distance was 8.4 cm (WAXS) or 34 cm (SAXS). The capillary was placed inside a vertically aligned graphite tube with a transversal hole, allowing the incident X-ray beam to cross freely. The temperature of the graphite tube was controlled by a system formed by a thermocouple connected to a proportional integral-derivative (PID) controller and to a power supply, acting as a fast-response online oven ranging from room temperature to 350 °C.

### Methyl 3,4,5-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyl-1-oxy)-benzoate (**6**)<sup>[3,4]</sup>

Under argon, methyl gallate (**4**) (1.49 g, 8.10 mmol), 1-iodo,1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecane (**5**) (15.0 g, 25.5 mmol), tetrabutylammonium bromide (0.130 g, 0.47 mmol) and finely powdered, dry K<sub>2</sub>CO<sub>3</sub> (6.77 g, 48.6 mmol) were mixed in MIBK (21 mL) at room temperature under vigorous stirring. Under argon, the beige reaction mixture was heated under reflux and vigorous stirring for 6 h after which TLC and <sup>1</sup>H-NMR showed the presence of product **6** and excess iodide only. The yellow suspension was cooled to room temperature, MIBK (25 mL) was added and the yellow suspension was filtered using a glass filter. The off-white residue was washed with MIBK (2 × 25 mL). Methanol (300 mL) was added to the combined yellow filtrates giving rise to the formation of a white precipitate. Subsequently, the suspension was heated to reflux till complete dissolution. The beige solution was allowed to reach room temperature slowly affording a white precipitate. The precipitate was filtered over a Büchner funnel and the white residue was washed with methanol-MIBK 3:1 (v:v) (2 × 100 mL). Drying of the residue in a vacuum-oven yielded ester **6** as a white powder (10.8 g, 6.90 mmol, 85 %). *R<sub>f</sub>* = 0.41 (silica gel, ethyl acetate:heptane 1:3 (v:v)); m.p. 88.5

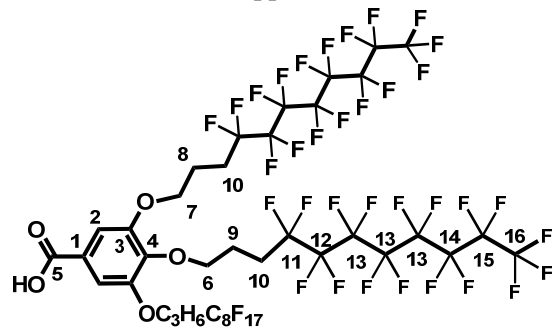
°C (Lit. 87-88 °C);<sup>[4]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.29 (s, 2H, 2), 4.12 (t, 4H, 7, <sup>3</sup>*J*(H,H) = 5.7 Hz), 4.06 (t, 2H, 6, <sup>3</sup>*J*(H,H) = 5.8 Hz), 3.91 (s, 3H, OCH<sub>3</sub>), 2.43-2.26 (6H, 10), 2.19-2.09 (m, 4H, 8),<sup>[5]</sup> 2.07-1.98 ppm (m, 2H, 9); <sup>13</sup>C NMR<sup>[6]</sup> (100 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 166.4, 152.2, 141.5, 125.6, 108.3, 71.9, 67.6, 52.3, 27.8 (t, <sup>2</sup>*J*(C,F) = 22.1 Hz), 21.5, 20.6 ppm; <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>):<sup>[7][8]</sup>  $\delta$  = -80.9 (t, 6F, <sup>3</sup>*J*(F,F) = 10.2 Hz, 16), -81.0 (t, 3F, <sup>3</sup>*J*(F,F) = 10.2 Hz, 16), -114.5 (tt, 4F, *J* = 16.7 and



15.5 Hz, 11),<sup>[9]</sup> -114.8 (tt, 2F,  $J = 16.6$  and  $15.3$  Hz, 11), -121.8--122.0 (18F, 13), -122.9 (6F, 14), -123.6 (6F, 12), -126.2--126.3 ppm (6F, 15), FT-IR (ATR):  $\nu$  (cm<sup>-1</sup>) = 2957, 2888, 1712 (C=O), 1587, 1502, 1479, 1441, 1432, 1382, 1373, 1344, 1197, 1144, 1114, 1060, 1031, 1010, 973, 937, 902, 865, 830, 769, 748, 740, 721, 705, 685, 656; MALDI-TOF MS:  $m/z$ : calcd for: 1564.07; found: 1563.94 ( $M^{*+}$ ), 1586.90 ( $M+Na^+$ ); Analysis: calcd (%) for C<sub>41</sub>H<sub>23</sub>F<sub>51</sub>O<sub>5</sub>: C 31.48, H 1.48; found: C 31.38, H 1.39.

### 3,4,5-Tris(1H,1H,2H,2H,3H,3H-perfluoroundecyl-1-oxy)-benzoic acid (7)

Under argon, methyl ester **6** (10.0 g, 6.39 mmol) was suspended in ethanol (50 mL) under vigorous stirring at room temperature after which a solution of NaOH (0.760 g, 19.0 mmol) in water (2 mL) was added. The white suspension was refluxed under stirring and argon for 5.5 h after which TLC and FT-IR showed the absence of starting material. Subsequently, ice-water was added which caused the formation of a thick suspension. Then, aqueous HCl (3 M, 7 mL) was added to the suspension under vigorous stirring to adjust the pH at 1-2. The thick, white suspension was filtered over a Büchner funnel and the residue was washed thoroughly with water (4 × 30 mL) and water-methanol 1:1 (v:v) (3 × 30 mL). Drying of the residue in a vacuum-oven yielded benzoic acid **7** as a white powder (9.55 g, 6.16 mmol, 96 %).  $R_f = 0.29$  (silica gel, ethyl acetate:heptane 1:1 (v:v)); m.p. 187-198 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> + HFIP-D<sub>2</sub>, 25 °C):  $\delta = 7.27$  (s, 2H, 2), 4.15-4.10 (6H, 6+7), 2.38-2.26 (m, 6H, 10), 2.20-2.10 (m, 4H, 8), 2.09-2.00 ppm (m, 2H, 9); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub> + HFIP-D<sub>2</sub>, 25 °C):  $\delta = 171.5, 152.6, 141.2, 126.0, 108.6, 73.2, 68.0, 27.9$  (t, <sup>2</sup> $J$ (C,F) = 22.5 Hz), 21.3, 20.6 ppm; <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub> + HFIP-D<sub>2</sub>):  $\delta = -81.9$  (t, 6F, <sup>3</sup> $J$ (F,F) = 10.2 Hz, 16),



-82.0 (t, 3F, <sup>3</sup> $J$ (F,F) = 10.1 Hz, 16), -115.0 (tt, 6F,  $J = 23.3$  and  $15.6$  Hz, 11),<sup>[10]</sup> -122.4--122.6 (18F, 13), -123.5 (6F, 14), -124.1 (6F, 12), -127.0 ppm (6F, 15); FT-IR (ATR):  $\nu$  (cm<sup>-1</sup>) = 2960, 2888, 1691 (C=O), 1589, 1506, 1478, 1433, 1372, 1333, 1199, 1146, 1135, 1115, 1029, 1006, 972, 866, 828, 777, 747, 739, 722, 704, 686, 656; MALDI-TOF MS:  $m/z$ : calcd: 1550.06; found: 1550.01 ( $M^{*+}$ ), 1573.99 ( $M+Na^+$ ); Analysis: calcd (%) for C<sub>40</sub>H<sub>21</sub>F<sub>51</sub>O<sub>5</sub>: C 30.99, H 1.37; found: C 30.90, H 1.19.

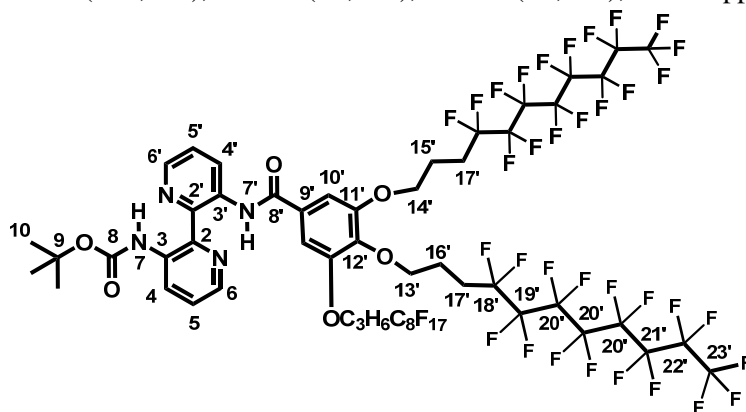
### 3,4,5-Tris(1H,1H,2H,2H,3H,3H-perfluoroundecyl-1-oxy)-benzoyl chloride (8)

Under argon, benzoic acid **7** (6.00 g, 3.87 mmol) was suspended in distilled dichloromethane (36 mL) and MNFB (48 mL) at room temperature after which oxalyl chloride (0.55 mL, 0.81 g, 6.4 mmol) and DMF (4 drops) were added under the escape of gases from the mixture. The bubbling suspension was stirred for an additional 2 h at room temperature during which the beige suspension dissolved. After confirmation by FT-IR spectroscopy of complete product formation, the solution was concentrated *in vacuo* and dried thoroughly on a high vacuum line to remove volatile residues yielding a beige residue (**8**) (6.07 g) that was used as such. FT-IR (ATR):  $\nu$  (cm<sup>-1</sup>) = 2961, 2890, 1746 (C=O), 1590, 1499, 1475, 1451, 1431, 1382, 1372, 1332, 1198, 1144, 1135, 1115, 1060, 1030, 1004, 974, 918, 864, 820, 790, 769, 740, 721, 704, 656.

### 3'-Tertiary-butoxycarbonylamino-3-[3,4,5-tris(1H,1H,2H,2H,3H,3H-perfluoroundecyl-1-oxy)benzoylamino]-2,2'-bipyridine (10)

Under argon, a solution of acid chloride **8** (6.07 g, 3.87 mmol) in dichloromethane (10 ml) and MNFB (30 ml) was added dropwise to a solution of 3'-tertiary-butoxycarbonylamino-2,2'-bipyridine-3-amine (**9**) (1.33 g, 4.64 mmol) and triethylamine (0.67 mL, 0.47 g, 4.64 mmol) in dichloromethane (30 ml) and MNFB (10 ml) under stirring at room temperature. The obtained thick yellowish suspension was refluxed for an additional 2 h and then stirred overnight at room temperature. Acetone (150 mL) and methanol (100 mL) were added and subsequently the formed yellowish suspension was heated under reflux for 30 min.<sup>[11]</sup> Then,

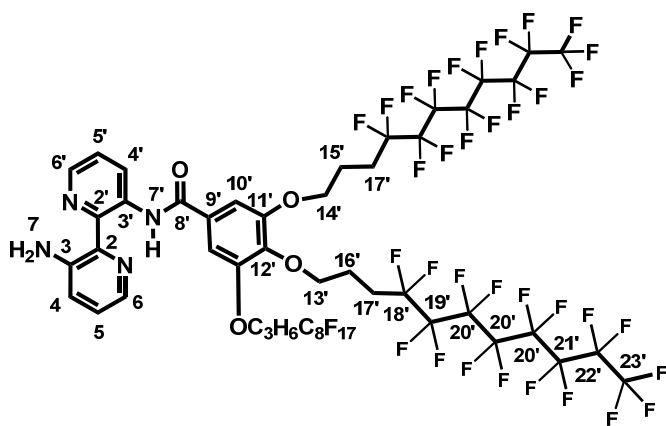
cooling of the suspension to room temperature yielded more precipitate. The suspension was filtered over a Büchner funnel and the obtained residue was washed with acetone-methanol 2:1 (v:v) (2 × 75 mL) yielding BOC protected **10** (6.27 g, 3.45 mmol, 90 %) as an off-white, sticky product after drying in a vacuum-oven.  $R_f = 0.71$  (silica gel, ethyl acetate:MNFB:CHCl<sub>3</sub> 1:2:5 (v:v:v)); m.p. 133.4 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> + HFIP-D<sub>2</sub> + C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>, 25 °C):  $\delta = 14.08$  (s, 0.1H, 7'),<sup>[12]</sup> 14.05 (s, 0.2H, 7'),<sup>[12]</sup> 12.27 (s, 0.1H, 7'),<sup>[12]</sup> 12.23 (s, 0.2H, 7'),<sup>[12]</sup> 9.06 (d, 1H, 4', <sup>3</sup>J(H,H) = 8.3 Hz), 8.73 (d, 1H, 4', <sup>3</sup>J(H,H) = 8.3 Hz), 8.45 (s, 1H, 6'), 8.23 (s, 1H, 6), 7.46-7.43 (dd, 1H, <sup>3</sup>J(H,H) = 8.5 Hz and <sup>3</sup>J(H,H) = 4.5 Hz, 5'), 7.37-7.35 (dd, <sup>3</sup>J(H,H) = 8.3 Hz and <sup>3</sup>J(H,H) = 4.4 Hz, 1H, 5), 7.20 (s, 2H, 10'), 4.16-4.12 (6H, 13'+14'), 2.39-2.29 (m, 6H, 17'), 2.22-2.14 (m, 4H, 15'), 2.11-2.03 (m, 2H, 16'), 1.54 ppm (s, 9H, BOC-H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub> + HFIP-D<sub>2</sub>, 25 °C):<sup>[13]</sup>  $\delta = 167.9, 154.5, 152.7, 143.5, 142.9, 140.6, 140.4, 136.2, 134.9, 131.2, 130.5, 130.3, 124.5, 124.4, 106.0, 82.7, 72.6, 67.8, 27.8, 27.5$  (t, <sup>2</sup>J(C,F) = 21.2 Hz), 21.1, 20.4 ppm; <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub> + HFIP-D<sub>2</sub>):  $\delta = 81.6$  (t, 6F, <sup>3</sup>J(F,F) = 9.9 Hz, 23'), -81.7 (t, 3F, <sup>3</sup>J(F,F) = 9.9 Hz, 23'), -115.0--115.1 (6F, 18'), -122.4 (18F, 20'), -123.3 (6F, 21'), -124.0 (6F, 19'), -126.8 ppm (6F, 22');



1723 (C=O carbamate), 1660 (C=O amide), 1584, 1569, 1495, 1452, 1438, 1371, 1336, 1295, 1199, 1147, 1115, 1046, 1030, 1014, 976, 905, 856, 842, 805, 769, 750, 733, 722, 704, 685, 658; MALDI-TOF MS:  $m/z$ : calcd: 1818.19; found: 1818.10 ( $M^{+}$ ), 1819.11 ( $M+H^{+}$ ), 1841.09 ( $M+Na^{+}$ ), 1857.07 ( $M+K^{+}$ ); Analysis: calcd (%) for C<sub>55</sub>H<sub>37</sub>F<sub>51</sub>N<sub>4</sub>O<sub>6</sub>: C 36.32, H 2.05, N 3.08; found: C 36.18, H 1.81, N 3.04.

### 3'-[3,4,5-Tris(1H,1H,2H,2H,3H,3H-perfluoroundecyl-1-oxy)benzoylamino]-2,2'-bipyridine-3-amine (11)

Under argon, BOC-protected compound **10** (6.00 g, 3.30 mmol) was dissolved in TFA (46 mL) and the yellowish solution was then stirred under bubbling of argon at room temperature until all starting material was converted according to TLC. The reaction mixture was concentrated *in vacuo* at room temperature<sup>[14]</sup> to give a yellow residue which was suspended in acetone (150 mL) and chilled in an ice-bath. Triethylamine (30 mL) dissolved in acetone (50 mL) was added dropwise to the yellow suspension under vigorous stirring giving a sticky, beige suspension. After stirring for an additional 30 min, the beige suspension was filtered over a Büchner funnel and the obtained residue was re-suspended in acetone (150 mL) and refluxed for 30 min under stirring. Then, the beige suspension was allowed to reach room temperature and filtered over a

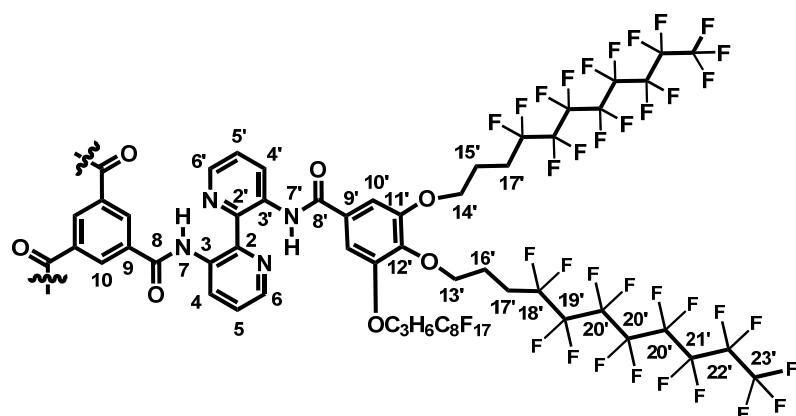


Büchner funnel and the residue was washed with acetone (2 × 50 mL). Drying of this residue in a vacuum-oven yielded amine **11** (5.01 g, 2.91 mmol, 88 %) as a beige compound.  $R_f = 0.57$  (silica gel, ethyl acetate:MNFB:CHCl<sub>3</sub> 1:2:5 (v:v:v)); m.p. 125.9 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub> + HFIP-D<sub>2</sub>, 25 °C):  $\delta = 12.16$  (bs, 1H, 7 N-H), 8.74 (d, 1H, 4', <sup>3</sup>J(H,H) = 8.4 Hz), 8.43 (d, 1H, 6', <sup>3</sup>J(H,H) = 4.6 Hz), 8.00 (d, 1H, 6, <sup>3</sup>J(H,H) = 4.4 Hz), 7.49 (dd, 1H, 5', <sup>3</sup>J(H,H) = 8.2 Hz and 4.8 Hz), 7.31-7.23 (m, 2H, 4+5), 7.08 (s, 2H, 10'), 4.12 (t, 6H, 13'+14', <sup>3</sup>J(H,H) = 5.8 Hz),<sup>[15]</sup> 2.41-

2.26 (m, 6H, 17'), 2.16 (m, 4H, 15'), 2.05 ppm (m, 2H, 16');<sup>161</sup> <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub> + HFIP-D<sub>2</sub>, 25 °C): δ = 168.0, 153.0, 145.2, 144.1, 143.3, 140.8, 139.2, 137.8, 134.3, 132.2, 130.2, 127.4, 125.6, 124.6, 106.3, 72.9, 68.1, 27.9 (t, <sup>2</sup>J(C,F) = 22.9 Hz), 21.6, 20.8 ppm; <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub> + HFIP-D<sub>2</sub>): δ = -81.4 (t, 6F, <sup>3</sup>J(F,F) = 10.2 Hz, 23'), -81.5 (t, 3F, <sup>3</sup>J(F,F) = 9.9 Hz, 23'), -114.8--115.1 (6F, 18'), -122.1--122.4 (18F, 20'), -123.2 (6F, 21'), -124.0 (6F, 19'), -126.7 ppm (6F, 22'), FT-IR (ATR): ν (cm<sup>-1</sup>) = 3403 and 3288 (NH<sub>2</sub>), 2961, 2886, 1647 (C=O), 1585, 1573, 1522, 1498, 1472, 1454, 1428, 1400, 1372, 1336, 1296, 1199, 1146, 1114, 1066, 1029, 1010, 975, 933, 916, 865, 827, 796, 748, 733, 722, 704, 686, 658; MALDI-TOF MS: *m/z*: calcd: 1718.14; found: 1718.08 (*M*<sup>+</sup>), 1719.08 (*M*+H<sup>+</sup>), 1741.06 (*M*+Na<sup>+</sup>); Analysis: calcd (%) for C<sub>50</sub>H<sub>29</sub>F<sub>51</sub>N<sub>4</sub>O<sub>4</sub>: C 34.94, H 1.70, N 3.26; found: C 34.93, H 1.47, N 3.26.

***N,N',N''*-Tris(3{3'-[3,4,5-tris(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyl-1-oxy)benzoylamino]-2,2'-bipyridyl})benzene-1,3,5-tricarboxamide (1)**

Under argon, a solution of trimesyl chloride (0.162 g, 0.610 mmol) in distilled dichloromethane (6 mL) was added dropwise to a well-stirred suspension of amine **11** (3.16 g, 1.84 mmol) and triethylamine (0.40 mL, 0.29 g, 2.87 mmol) in dichloromethane (8 mL) and MNFB (55 mL). A white precipitate was formed. Then, the well-stirred, gray suspension was refluxed under argon for 4 h after which all acid chloride was converted according to FT-IR spectroscopy. After cooling to room temperature, methanol (50 mL) and acetone (50 mL) were added while stirring. The formed precipitate was filtered over a Büchner funnel and the residue was washed with acetone-methanol 1:1 (v:v) (2 × 25 mL) and resuspended in CHCl<sub>3</sub> (90 mL), triethylamine (5 mL) and MNFB (30 mL) followed by reflux for 30 min. Subsequently, the beige suspension was allowed to reach room temperature and filtered over a Büchner funnel. The beige residue was washed with CHCl<sub>3</sub>-MNFB 3:1 (v:v) (2 × 15 mL). This procedure was repeated once more to yield a sticky, beige residue (2.3 g) that contained predominantly desired product **1** according to <sup>1</sup>H-NMR. The crude product was further purified by repetitive recrystallisations from a hot mixture of chloroform (10 mL), acetone (10 mL) and MNFB (35 mL) and subsequent column chromatography (silica gel, HFIP:CHCl<sub>3</sub>:MNFB 1:10:9 (v:v:v)) as eluent) after which discotic **1** was obtained as a white, sticky solid (1.47 g, 0.277 mmol, 48 %). *R*<sub>f</sub> = 0.40 (silica gel, HFIP:CHCl<sub>3</sub>:MNFB 1:10:9 (v:v:v)); m.p. > 375 °C (degrades); <sup>1</sup>H NMR (400 MHz, 3.8 mM, CDCl<sub>3</sub> + 25 vol% HFIP + 25 vol% HFIP-D<sub>2</sub>, 25 °C): 15.26 (s, 0.75H, 7),<sup>[17]</sup> 15.23 (s, 0.75H, 7),<sup>[17]</sup> 14.44 (s, 0.75H, 7'),<sup>[17]</sup> 14.40 (s, 0.75H, 7'),<sup>[17]</sup> 9.21 (d, 3H, 4, <sup>3</sup>J(H,H) = 8.3 Hz), 9.05 (s, 3H, 10), 9.01 (d, 3H, 4', <sup>3</sup>J(H,H) = 8.3 Hz), 8.65 (d, 3H, 6', <sup>3</sup>J(H,H) = 4.8 Hz), 8.43 (d, 3H, 6, <sup>3</sup>J(H,H) = 4.1 Hz), 7.56 (dd, 3H, 5', <sup>3</sup>J(H,H) = 8.5 Hz and <sup>3</sup>J(H,H) = 4.8 Hz), 7.46 (dd, 3H, 5, <sup>3</sup>J(H,H) = 8.6 Hz and <sup>3</sup>J(H,H) = 4.6 Hz), 7.21 (s, 6H, 10'), δ = 4.21-4.16 (m, 18H, 13'+14'), 2.44-2.29 (m, 18H, 17'), 2.25-2.16 (m, 12H, 15'), 2.14-2.05 ppm (m, 6H, 16'); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub> + HFIP-D<sub>2</sub>, 25 °C): δ = 168.9, 168.8, 166.0, 153.2, 143.4, 142.8,



142.3, 140.7, 136.8, 136.5, 136.3, 131.5, 131.4, 131.3, 131.2, 130.3, 125.1, 125.0, 106.5, 73.4, 68.4, 27.9 (t, <sup>2</sup>J(C,F) = 22.7 Hz), 21.4, 20.8 ppm; <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub> + HFIP-D<sub>2</sub>): δ = -81.9--81.9 (27F, 23'), -115.1--115.2 (18F, 18'), -122.3--122.6 (54F, 20'), -123.4 (18F, 21'), -124.2 (18F, 19'), -127.0 ppm (18F, 22'), FT-IR (ATR): ν (cm<sup>-1</sup>) = 2961, 1671, 1581, 1517, 1469, 1446, 1429, 1370, 1331, 1298, 1198, 1145, 1134, 1115, 1075, 1030, 1016,

974, 914, 864, 826, 800, 779, 743, 730, 717, 704, 673, 656; MALDI-TOF MS:  $m/z$ : calcd: 5311.40; found: 5312.41 ( $M+H^+$ ), 5334.65 ( $M+Na^+$ ), 5351.03 ( $M+K^+$ ), 5375.59 ( $M+Cu^+$ ); Analysis: calcd (%) for  $C_{159}H_{87}F_{153}N_{12}O_{15}$ : C 35.95, H 1.65, N 3.16; found: C 35.96, H 1.46, N 3.33.

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- [5] For these protons a quintet was expected but six lines are observed; probably due to an additional  $^4J(H,F)$  coupling or due to the coupling with two different neighboring  $CH_2$  groups.
- [6] The perfluorinated carbons can be observed as multiplets between 105 and 125 ppm, but can not be resolved due to their coupling with the  $^{19}F$  nucleus.
- [7]  $^{19}F$  NMR assignment of the perfluorinated tails according to: Marchione, A. A.; Buck, R. C. *Magn. Reson. Chem.* **2009**, *47*, 194 and Battiste, J. L.; Jing, N.; Newmark, R. A. *J. Fluorine Chem.* **2004**, *125*, 1331.
- [8] Surprisingly, the  $CF_3$ -group bears the least shielded fluorines and the  $CF_2$ -group next to the  $CF_3$ -group bears the most shielded fluorines.
- [9] These fluorines are coupled with a neighboring-  $CH_2$ - and - $CF$ - group, however assignment of the coupling constants was not possible.
- [10] Instead of two triplet-of-triplets as observed for ester **6**, a single triplet-of-triplet was observed, presumably due to the presence of a fluorinated solvent.
- [11] Due to the fast formation of a lot of foam from boiling solutions of BOC protected **10** or from amine **11** care has to be taken during recrystallization steps or concentration *in vacuo*.
- [12] Due to the partial exchange of the acidic amide and carbamate protons with deuterium splitting of the N-H protons is observed together with a reduced intensity of the signal in proton NMR.
- [13] Some aromatic signals may overlap with the signals originated from the fluorinated carbons or HFIP.
- [14] Heating of a TFA salt of an amine can cause the formation of a TFA amide.
- [15] Surprisingly, only one triplet is observed; it can actually exist of two superimposed triplets belonging to 13' and 14' respectively.
- [16] In this case HFIP induces a significant upfield shift of the N-H proton and of proton 4' and vanishing of the  $NH_2$  protons compared to the chemical shifts of these protons of monoacylated compounds as reported in ref. [1].
- [17] Due to the partial exchange of the acidic amide protons with deuterium, splitting of the N-H protons is observed together with a reduced intensity of the signal in proton NMR.