Supramolecular organization of liquid-crystal dimers - *bis*-cyanobiphenyl alkanes on HOPG by scanning tunneling microscopy†

Klaudyna Krzyżewska,[a] Tomasz Jaroch,[a] Agnieszka Maranda-Niedbała,[a] Damian Pociecha,[b] Ewa Górecka,[b] Ziauddin Ahmed,[c] Chris Welch,[c] Georg H Mehl,[c] Adam Proń,[d] Robert Nowakowski[a]*

[a]Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warsaw 01-224, Poland; [b]Warsaw University, Faculty of Chemistry, Żwirki i Wigury 101, Warsaw 02-089, Poland; [c]School of Mathematics & Physical Sciences, University of Hull, Cottingham Road, Hull, HU6 7RX, UK; [d]Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland

Electronic Supplementary Information

Identification of the investigated materials

NMR were recorded in deuterated solvents on a Jeol JNM ECP400 spectrometer, with chemical shifts reported relative to either TMS δ_H = 0 as the internal standard or residual solvent [$CDCl_3$, δ_H = 7.26, δ_C =77.0 ppm ; CD_2Cl_2, δ_H = 5.32 ppm, δ_C =77.0 ppm]. NMR were recorded at 400 MHz, 100.5 MHz and 376 MHz for ^{1}H, ^{13}C and ^{19}F respectively. Chemical shifts are given in ppm and coupling constants (J) are given in Hertz (Hz) and splittings are defined as listed below.

s : singlet d : doublet t : triplet m : multiplet

Low resolution electron ionisation (EI), electro-spray (ES), chemical ionisation (CI), matrix assisted laser deposition ionisation (MALDI) and high resolution mass spectrometry (HRMS)

were obtained via the EPSRC National Mass Spectrometry Service Centre at Swansea University, Wales.

The purity of the compounds was confirmed by high performance liquid chromatography. The HPLC setup consisted of Gilson 321 pump, Agilent/HP1100 detector with a Phenomex LUNA 18(2) reverse phase C18 column. The column dimensions are 250 mm x 4.6 mm, 5 µm particles and 100 Å pore size, with Unipoint software. All HPLC was performed using 1:1 acetonitrile-dichloromethane at 1 ml.min^{-1} unless otherwise specified.

All of the investigated materials have been reported before and are literature known. The final products were synthesised according to previously reported and discussed routes and methods [1]
The LC transitions and properties of the reported systems have either recently been reported [1] or reviewed [2,3].
The results from the chemical analysis of the final products are listed below.

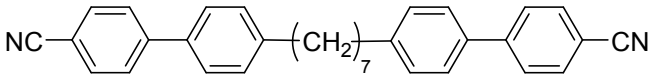
[1] Z. Ahmed, C.Welch and G. H. Mehl, The design and investigation of the self assembly of dimers with two nematic phases, *RSC Advances*, 2015, **5**, 113, 93513-93521

[2] V.N. Panov, J.K. Vij, G.H. Mehl, The Twist Bend Nematic Phase in Cyanobiphenyls and Difluoroterphenyls Bimesogens, Liquid Crystals 2017, **44**, 147-159

[3] Z. Ahmed, PhD thesis, The design, synthesis and properties of dimeric molecules exhibiting nematic-nematic transitions, University of Hull, November 2014.

List of materials

CB7CB



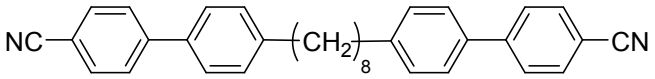
δ_H(400MHz; CD_2Cl_2) 7.74-7.68 (m, 8H), 7.53 (d, ^3J = 8.3 Hz, 4H), 7.30 (d, ^3J = 8.3 Hz, 4H), 2.66 (t, ^3J = 7.3 Hz, 4H), 1.71-1.59 (m, 4H), 1.42-1.33 (m, 6H)

δ_C(100MHz; CD_2Cl_2) 145.81, 144.24, 136.76, 132.96, 129.53, 127.76, 127.38, 119.32, 110.92, 35.89, 31.75, 29.67, 29.56

MS (ASAP) *m/z* 455.2 $(M+H)^+$
HRMS : calculated for $C_{33}H_{31}N_2$: 455.2487, found 455.2487

Assay (HPLC, C_{18}, MeCN:DCM 1:1) = 99.8 %

CB8CB



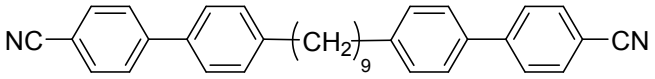
δ_H(400MHz; CD_2Cl_2) 7.74-7.68 (m, 8H), 7.54 (d, ^3J = 8.3 Hz, 4H), 7.30 (d, ^3J = 8.3 Hz, 4H), 2.66 (t, ^3J = 7.8 Hz, 4H), 1.69-1.59 (m, 4H), 1.39-1.33 (m, 8H)

δ_C(100MHz; CD_2Cl_2) 145.83, 144.27, 136.77, 132.96, 129.54, 127.77, 127.38, 119.33, 110.93, 35.92, 31.80, 29.79, 29.67

MS (ASAP) *m/z* 469.3 $(M+H)^+$
HRMS : calculated for $C_{34}H_{33}N_2$: 469.2644, found 469.2643

Assay (HPLC, C_{18}, MeCN:DCM 1:1) = 99.5 %

CB9CB



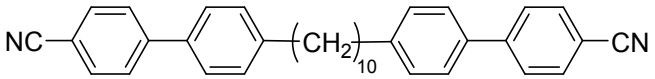
δ_H(400MHz; CD_2Cl_2) 7.74-7.68 (m, 8H), 7.53 (d, ^3J = 8.3 Hz, 4H), 7.30 (d, ^3J = 8.3 Hz, 4H), 2.65 (t, ^3J = 7.4 Hz, 4H), 1.67-1.59 (m, 4H), 1.39-1.28 (m, 10H)

δ_C(100MHz; CD_2Cl_2) 145.83, 144.29, 136.76, 132.96, 129.54, 127.77, 127.38, 119.33, 110.92, 35.93, 31.81, 29.87, 29.83, 29.66

MS (ASAP) *m/z* 483.3 $(M+H)^+$
HRMS : calculated for $C_{35}H_{35}N_2$: 483.2800, found 483.2800

Assay (HPLC, C_{18}, MeCN:DCM 1:1) = 99.5 %

CB10CB



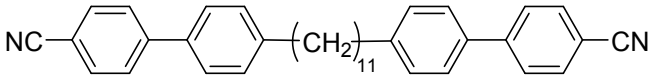
δ_H(400MHz; CD_2Cl_2) 7.75-7.67 (m, 8H), 7.53 (d, ^3J = 8.3 Hz, 4H), 7.30 (d, ^3J = 8.3 Hz, 4H), 2.65 (t, ^3J = 7.3 Hz, 4H), 1.70-1.59 (m, 4H), 1.40-1.25 (m, 12H)

δ_C(100MHz; CD_2Cl_2) 145.83, 144.30, 136.75, 132.96, 129.54, 127.77, 127.38, 119.33, 110.92, 35.94, 31.83, 29.95, 29.87, 29.70

MS (ASAP) *m/z* 497.3 $(M+H)^+$
HRMS : calculated for $C_{36}H_{37}N_2$: 497.2957, found 497.2954

Assay (HPLC, C_{18}, MeCN:DCM 1:1) = 99.4 %

CB11CB



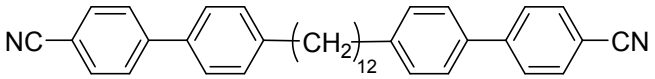
δ_H(400MHz; CD_2Cl_2) 7.74-7.68 (m, 8H), 7.54 (d, ^3J = 8.3 Hz, 4H), 7.30 (d, ^3J = 8.3 Hz, 4H), 2.65 (t, ^3J = 7.8 Hz, 4H), 1.69-1.59 (m, 4H), 1.40-1.25 (m, 14H)

δ_C(100MHz; CD_2Cl_2) 145.83, 144.31, 136.75, 132.96, 129.54, 127.77, 127.38, 119.33, 110.91, 35.94, 31.83, 30.00, 29.95, 29.87, 29.70

MS (ASAP) *m/z* 511.3 $(M+H)^+$
HRMS : calculated for $C_{37}H_{39}N_2$: 511.3113, found 511.3112

Assay (HPLC, C_{18}, MeCN:DCM 1:1) = 99.4 %

CB12CB



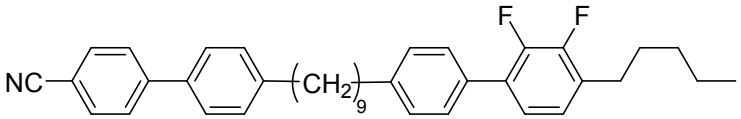
δ_H(400MHz; CD_2Cl_2) 7.74-7.68 (m, 8H), 7.53 (d, ^3J = 8.3 Hz, 4H), 7.30 (d, ^3J = 8.3 Hz, 4H), 2.65 (t, ^3J = 7.3 Hz, 4H), 1.70-1.58 (m, 4H), 1.40-1.25 (m, 16H)

δ_C(100MHz; CD_2Cl_2) 145.85, 144.32, 136.76, 132.97, 129.54, 127.77, 127.38, 119.34, 110.92, 35.94, 31.83, 30.02, 29.97, 29.88, 29.70

MS (ASAP) *m/z* 525.3 $(M+H)^+$
HRMS : calculated for $C_{38}H_{41}N_2$: 525.3270, found 525.3271

Assay (HPLC, C_{18}, MeCN:DCM 1:1) = 99.4 %

CB9DFCB



δ_H(400MHz; CD_2Cl_2) 7.68 (m, 4H), 7.50 (d, ^3J = 8.16 Hz, 2H), 7.44 (dd, ^3J = 6.5 Hz, ^4J = 1.5 Hz, 2H), 7.26 (m, 4H), 7.08 (dt, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 1H), 6.96 (dt, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 1H), 2.65 (m, 6H), 1.63-1.50 (m, 6H), 1.42-1.26 (m, 14H), 0.88 (t, ^3J = 6.8 Hz, 3H)

δ_C(100MHz; $CDCl_3$) 145.6, 143.8, 142.7, 136.5, 132.6, 129.2, 128.70, 128.68, 128.6, 127.5, 127.0, 124.6, 124.1, 119.1, 110.5, 35.7, 35.6, 31.46, 31.38, 29.7, 29.5, 29.32, 29.28, 28.7, 22.5, 14.0

δ_F (376 MHz; $CDCl_3$) -143.7 (dd, ^3J(F-F) = 20.8 Hz, ^4J(F-H) = 6.9 Hz), -144.3 (dd, ^3J(F-F) = 20.8 Hz, ^4J(F-H) = 6.9 Hz)

MS (CI) 564 $(M+H)^+$
HRMS : calculated for $C_{39}H_{44}F_2N$: 564.3441, found 564.3425

Assay (HPLC, C18, MeCN:DCM 80:20) = 99.4 %