Supramolecular organization of liquid-crystal dimers -

*bis*-cyanobiphenyl alkanes on HOPG by scanning
tunneling microscopy†

Klaudyna Krzyżewska,† Tomasz Jaroch,† Agnieszka Maranda-Niedbała,‡ Damian Pociecha,‡
Ewa Górecka,§ Ziauddin Ahmed,∥ Chris Welch,∥ Georg H Mehl,∥ Adam Proń,¶ Robert
Nowakowski**

†Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warsaw 01-
224, Poland; ‡Warsaw University, Faculty of Chemistry, Żwirki i Wigury 101, Warsaw 02-
089, Poland; ∥School of Mathematics & Physical Sciences, University of Hull, Cottingham
Road, Hull, HU6 7RX, UK; ¶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 ¹H, ¹³C and ¹⁹F 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.


**List of materials**

**CB7CB**

\[
\text{NC} - \begin{array}{c}
\begin{array}{c}
\text{(CH}_2\text{)}_7 \\
\text{C}
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{c}
\text{NC}
\end{array}
\end{array}
\text{-CN}
\]

$\delta$ (400MHz; CD$_2$Cl$_2$) 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)

$\delta$ (100MHz; CD$_2$Cl$_2$) 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**

\[
\text{NC} - \begin{array}{c}
\begin{array}{c}
\text{(CH}_2\text{)}_8 \\
\text{C}
\end{array}
\end{array} - \begin{array}{c}
\begin{array}{c}
\text{NC}
\end{array}
\end{array}
\text{-CN}
\]
\[\delta_H (400\text{MHz}; \text{CD}_2\text{Cl}_2) \ 7.74-7.68 \ (m, 8\text{H}), \ 7.54 \ (d, ^3J = 8.3 \text{ Hz}, 4\text{H}), \ 7.30 \ (d, ^3J = 8.3 \text{ Hz}, 4\text{H}), \ 2.66 \ (t, ^3J = 7.8 \text{ Hz}, 4\text{H}), \ 1.69-1.59 \ (m, 4\text{H}), \ 1.39-1.33 \ (m, 8\text{H})\]

\[\delta_C (100\text{MHz}; \text{CD}_2\text{Cl}_2) \ 145.83, 144.27, 136.77, 132.96, 129.54, 127.77, 127.38, 119.33, 110.93, 35.92, 31.80, 29.79, 29.67\]

**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**

\[
\text{NC}-
\begin{array}{ccccccc}
  & & & & & & \\
  & & & & & & \\
  & & & & & & \\
  & & & & & & \\
\end{array}
\]

\[\delta_H (400\text{MHz}; \text{CD}_2\text{Cl}_2) \ 7.74-7.68 \ (m, 8\text{H}), \ 7.53 \ (d, ^3J = 8.3 \text{ Hz}, 4\text{H}), \ 7.30 \ (d, ^3J = 8.3 \text{ Hz}, 4\text{H}), \ 2.65 \ (t, ^3J = 7.4 \text{ Hz}, 4\text{H}), \ 1.67-1.59 \ (m, 4\text{H}), \ 1.39-1.28 \ (m, 10\text{H})\]

\[\delta_C (100\text{MHz}; \text{CD}_2\text{Cl}_2) \ 145.83, 144.29, 136.76, 132.96, 129.54, 127.77, 127.38, 119.33, 110.92, 35.93, 31.81, 29.87, 29.83, 29.66\]

**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**

\[
\text{NC}-
\begin{array}{ccccccc}
  & & & & & & \\
  & & & & & & \\
  & & & & & & \\
  & & & & & & \\
\end{array}
\]

\[\delta_H (400\text{MHz}; \text{CD}_2\text{Cl}_2) \ 7.75-7.67 \ (m, 8\text{H}), \ 7.53 \ (d, ^3J = 8.3 \text{ Hz}, 4\text{H}), \ 7.30 \ (d, ^3J = 8.3 \text{ Hz}, 4\text{H}), \ 2.65 \ (t, ^3J = 7.3 \text{ Hz}, 4\text{H}), \ 1.70-1.59 \ (m, 4\text{H}), \ 1.40-1.25 \ (m, 12\text{H})\]

\[\delta_C (100\text{MHz}; \text{CD}_2\text{Cl}_2) \ 145.83, 144.30, 136.75, 132.96, 129.54, 127.77, 127.38, 119.33, 110.92, 35.94, 31.83, 29.95, 29.87, 29.70\]

**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**

\[
\text{NC}-
\begin{array}{ccccccc}
  & & & & & & \\
  & & & & & & \\
  & & & & & & \\
  & & & & & & \\
\end{array}
\]

\[\delta_H (400\text{MHz}; \text{CD}_2\text{Cl}_2) \ 7.74-7.68 \ (m, 8\text{H}), \ 7.54 \ (d, ^3J = 8.3 \text{ Hz}, 4\text{H}), \ 7.30 \ (d, ^3J = 8.3 \text{ Hz}, 4\text{H}), \ 2.65 \ (t, ^3J = 7.8 \text{ Hz}, 4\text{H}), \ 1.69-1.59 \ (m, 4\text{H}), \ 1.40-1.25 \ (m, 14\text{H})\]
\[ \delta_c(100\text{MHz}; \text{CD}_2\text{Cl}_2) \quad 145.83, 144.31, 136.75, 132.96, 129.54, 127.77, 127.38, 119.33, 110.91, 35.94, 31.83, 30.00, 29.95, 29.87, 29.70 \]

**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 %**

\[ \text{CB12CB} \]

\[ \text{NC-} \quad \text{(CH}_2\text{)}_{12} \quad \text{NC} \]

\[ \delta_h(400\text{MHz}; \text{CD}_2\text{Cl}_2) \quad 7.74-7.68 \text{ (m, 8H)}, \quad 7.53 \text{ (d, } {^3}J = 8.3 \text{ Hz, 4H)}, \quad 7.30 \text{ (d, } {^3}J = 8.3 \text{ Hz, 4H)}, \quad 2.65 \text{ (t, } {^3}J = 7.3 \text{ Hz, 4H)}, \quad 1.70-1.58 \text{ (m, 4H)}, \quad 1.40-1.25 \text{ (m, 16H)} \]

\[ \delta_c(100\text{MHz}; \text{CD}_2\text{Cl}_2) \quad 145.85, 144.32, 136.76, 132.97, 129.54, 127.77, 127.38, 119.34, 110.92, 35.94, 31.83, 30.02, 29.97, 29.88, 29.70 \]

**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 %**

\[ \text{CB9DFCB} \]

\[ \text{NC-} \quad \text{(CH}_2\text{)}_{9} \quad \text{F} \quad \text{F} \quad \text{CN} \]

\[ \delta_h(400\text{MHz}; \text{CD}_2\text{Cl}_2) \quad 7.68 \text{ (m, 4H)}, \quad 7.50 \text{ (d, } {^3}J = 8.16 \text{ Hz, 2H)}, \quad 7.44 \text{ (dd, } {^3}J = 6.5 \text{ Hz, } {^4}J = 1.5 \text{ Hz, 2H)}, \quad 7.26 \text{ (m, 4H)}, \quad 7.08 \text{ (dt, } {^3}J = 7.5 \text{ Hz, } {^4}J = 1.6 \text{ Hz, 1H)}, \quad 6.96 \text{ (dt, } {^3}J = 7.5 \text{ Hz, } {^4}J = 1.6 \text{ Hz, 1H)}, \quad 2.65 \text{ (m, 6H)}, \quad 1.63-1.50 \text{ (m, 6H)}, \quad 1.42-1.26 \text{ (m, 14H)}, \quad 0.88 \text{ (t, } {^3}J = 6.8 \text{ Hz, 3H)} \]

\[ \delta_c(100\text{MHz}; \text{CDCl}_3) \quad 145.6, 143.8, 142.7, 136.5, 132.6, 129.2, 128.70, 128.68, 128.6, 127.5, 127.0, 124.6, 124.1, 119.1, 110.5, 35.7, 35.6, 31.46, 31.38, 29.7, 29.5, 29.32, 29.28, 28.7, 22.5, 14.0 \]

\[ \delta_f(376\text{ MHz}; \text{CDCl}_3) \quad -143.7 \text{ (dd, } {^3}J(F-F) = 20.8 \text{ Hz, } {^4}J(F-H) = 6.9 \text{ Hz)}, \quad -144.3 \text{ (dd, } {^3}J(F-F) = 20.8 \text{ Hz, } {^4}J(F-H) = 6.9 \text{ Hz)} \]

**MS (Cl) 564 (M+H)**

HRMS: calculated for C_{39}H_{44}F_2N: 564.3441, found 564.3425

**Assay (HPLC, C_{18}, MeCN:DCM 80:20) = 99.4 %**