Supplementary Material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information for

The Effect of Carborane, Bicyclo[2.2.2]octane and Benzene on Mesogenic and Dielectric Properties of Laterally Fluorinated Three-Ring Mesogens

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Table of Content:

1. Thermal Data

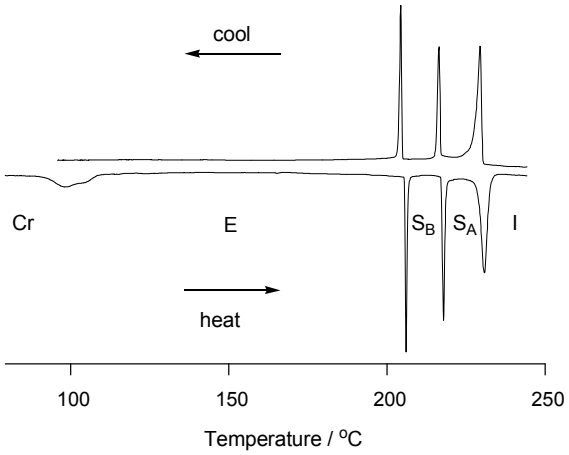


Figure 1. Partial heating and cooling DSC curves for **1D** recorded at a rate of 5 °C•min^{-1}.

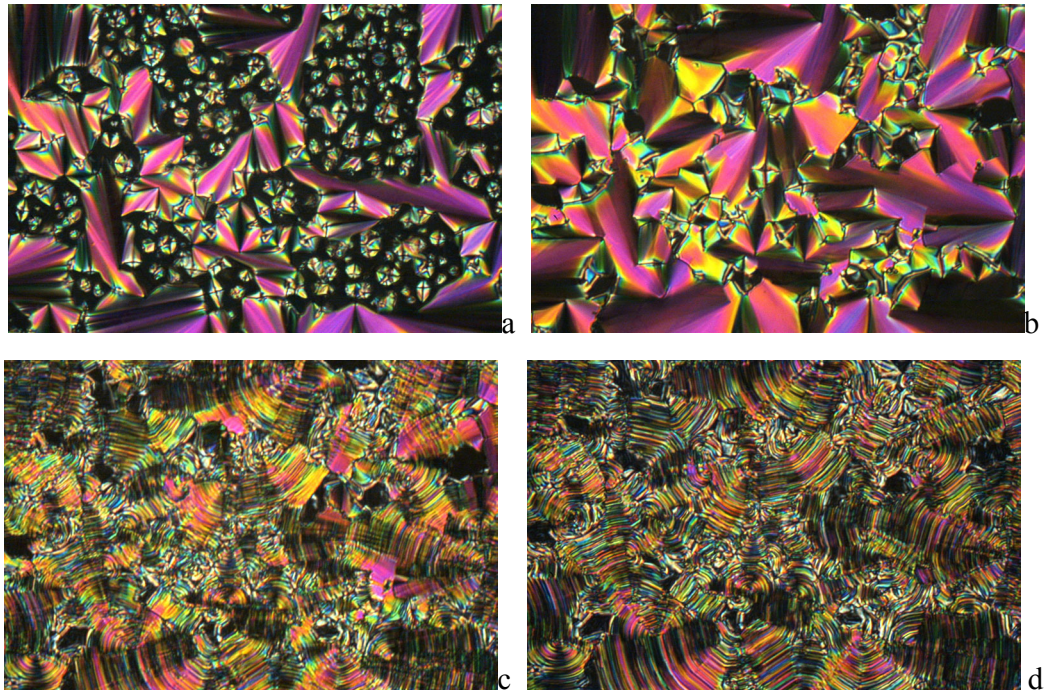


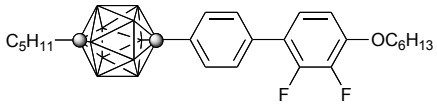
Figure 2. Natural textures observed in polarized light for **3D** in the same sample region: a) SmA growing from isotropic phase, b) SmB at ~190 °C, c) E phase at ~170 °C, d) glass at ~100 °C. Magnification 150×.

2. Dielectric Data

Dielectric parameters in Tables 1-4 for low concentration solutions of additives **2** to 6-CHBT were obtained from by averaging 10 measurements of each solution in a single cell. Standard

deviation of the resulting values ≤ ±0.02. Dielectric permittivity values for the host were obtained by averaging results for 3 cells with the std of ±0.1. All measurements were run at 25 ^{o}C. Error on concentration values ~1.5%

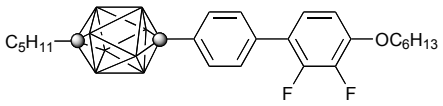
Table 1



2A

parameter	mole fraction			
	0.00 (host)	0.0458	0.0953	0.1493
$\varepsilon_{\parallel}$	11.0	10.53	10.08	9.50
$\varepsilon_{\perp}$	3.9	4.04	4.18	4.24
$\Delta\varepsilon$	7.1	6.49	5.91	5.27

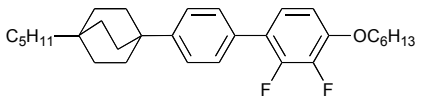
Table 2



2B

Parameter	mole fraction			
	0.00 (host)	0.0487	0.0995	0.1671
$\varepsilon_{\parallel}$	11.0	10.46	10.27	9.55
$\varepsilon_{\perp}$	3.9	4.00	4.11	4.45
$\Delta\varepsilon$	7.1	6.46	6.16	5.095

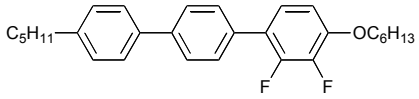
Table 3



2C

Parameter	mole fraction			
	0.00 (host)	0.0550	0.0953	0.1489
$\varepsilon_{\parallel}$	11.0	10.56	10.33	10.02
$\varepsilon_{\perp}$	3.9	3.97	4.12	4.33
$\Delta\varepsilon$	7.1	6.59	6.21	5.69

Table 4



2D

Parameter	mole fraction				
	0.00 (host)	0.0444	0.0724	0.1092	0.1498
$\varepsilon_{\parallel}$	11.0	10.90	10.48	10.29	10.16
$\varepsilon_{\perp}$	3.9	4.09	4.07	4.21	4.28
$\Delta\varepsilon$	7.1	6.80	6.40	6.07	5.88

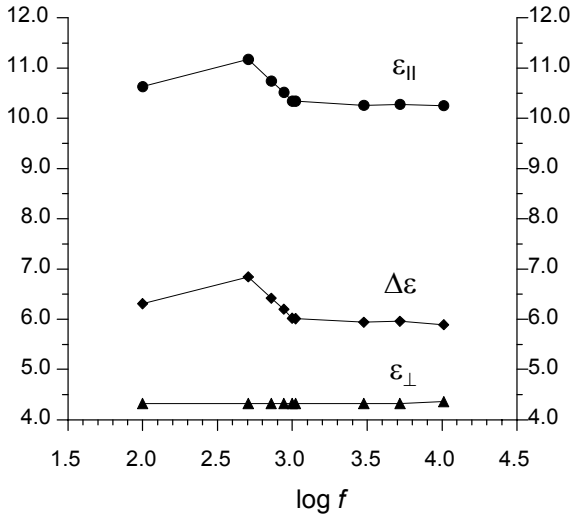


Figure 3. A plot of dielectric permittivity for a solution of **2A** in 6-CHBT as a function of frequency *f*.

3. Details for Calculations in the Nematic Phase

The Equations derived from the Maier-Meier theory used in this work were adopted from literature[1,2] and had the following form:

$$\Delta\varepsilon = \frac{NFh}{\varepsilon_0}\left\{\Delta\alpha - \frac{F\mu_{eff}^{\ 2}}{2k_BT}\left(1-3\cos^2\beta\right)\right\}S$$

$$\varepsilon_{\parallel} = 1 + \frac{NFh}{\varepsilon_0}\left\{\bar{\alpha} + \frac{2}{3}\Delta\alpha S + \frac{F\mu_{eff}^{\ 2}}{3k_BT}\left[1-\left(1-3\cos^2\beta\right)S\right]\right\}$$

$$\varepsilon_{\perp} = 1 + \frac{NFh}{\varepsilon_0}\left\{\bar{\alpha} - \frac{1}{3}\Delta\alpha S + \frac{F\mu_{eff}^{\ 2}}{3k_BT}\left[1+\frac{1}{2}\left(1-3\cos^2\beta\right)S\right]\right\}$$

All quantities were in SI units.

• Dielectric permittivity of vacuum:

$\varepsilon = 1.114\times10^{-10}/4\pi = 8.865\times10^{-12}$ F•m^{-1}.

• The matrix of electronic polarizabilities α in a.u. units listed in the output file for each molecule was diagonalized. The resulting principal values were converted to F•m^2 units by multiplying with

$1.482 \times 4\pi\varepsilon \times10^{-31} = 1.651\times10^{-41}$.

• Computed dipole moments μ in Debye were converted to dipole moments in C•m units using the conversion 1D = 3.3356×10^{-30} C•m.

• Number density N used in all calculations was obtained for each **2** assuming density of the liquid to be1000 kg•m^{-3}, and expressed in molecules per m^3.

• For calculations involving the extrapolated dielectric parameters for **2**, reaction field factors *F* and *h* were calculated for the pure host 6-CHBT using literature[3] values for $n_{\perp} = 1.5212$ and $n_{||} = 1.6610$ ($\tilde{n}^2 = 2.46$) and experimental average permittivity $\varepsilon_s = 5.93$. Thus, reaction field parameters $F = 1.335$ and $h = 1.383$ were obtained for 6-CHBT using the following equations:

$$F = \frac{(2\varepsilon_s+1)(n^2+2)}{3(2\varepsilon_s+n^2)} \qquad h = \frac{3\varepsilon_s}{(2\varepsilon_s+1)}$$

The former is a Dunmur-Toriyama expression for *F*.[4]

• Field parameters used in computations of the dielectric parameters for pure mesogens **2** were obtained according to the following equations:

$$F = \frac{1}{1 - \bar{\alpha} \bullet f} \quad \text{where} \quad f = \frac{2(\bar{\varepsilon}_s - 1)}{2\bar{\varepsilon}_s + 1} \bullet \frac{N}{3\varepsilon_0} \quad \text{and} \quad h = \frac{3\varepsilon_s}{(2\varepsilon_s + 1)}$$

Static permittivity ε_s was found by solving numerically the following equation for each molecule:[5]

$$\frac{NFh}{\varepsilon_0}\left(\bar{\alpha} + \frac{F\mu_{eff}^{\ 2}}{3k_B T}\right) - \varepsilon_s + 1 = 0$$

Table 5. Bulk order parameter *S* calculated for solutions of **2** in 6-CHBT according to:[a]

$$S = \frac{\Delta\varepsilon}{C \bullet x + C_{6CHBT} \bullet (1 - x)} \quad \text{where } C_{6CHBT} = 10.61$$

	C	$x_1 \times 10^3$	*S*	$x_2 \times 10^3$	*S*	$x_3 \times 10^3$	*S*
2A	-0.76	4.58	0.643	9.53	0.620	14.93	0.591
2B	-1.88	4.87	0.646	9.95	0.658	16.71	0.598
2C	-3.22	5.50	0.669	9.53	0.668	14.89	0.666
2D	-2.83	7.24	0.664	10.92	0.664	14.98	0.684

[a] The molecular factor C_{6CHBT} for 6-CHBT was calculated from the measured $\Delta\varepsilon$ = 7.11 and literature[1] temperature-dependent order parameter *S* = 0.67 at 25 °C. For computation of molecular factors *C* for each compound see the main text. $\Delta\varepsilon$ values for each mixture are reported in Tables 1-4.

4. Quantum-mechanical computational details.

Quantum-mechanical calculations were carried out using Gaussian 98[6] or MOPAC 6.0 suites of programs. Geometry optimizations for unconstrained conformers of **2** with the most

extended molecular shapes were undertaken at the AM1[7] (MOPAC 6), HF/6-31G(d), B3LYP/3-21G and B3LYP/6-31G(d) levels of theory using default convergence limits.

5. Selection of a quantum-mechanical computational method

In order to rationally select a computational method for analysis of results for **2**, dipole moments and electronic polarizabilities of several small molecules were investigated using semi-empirical, ab initio, and DFT methods (Tables 6 and 7). Semi-empirical methods are most cost effective, and two of them, AM1 and PM3, have been successfully used in computing dielectric properties of liquid crystals, [5,8] Both methods give reasonable molecular geometries, but only the AM1 method has been parameterized for the boron atom. This parametrization, however, is not optimum for boron clusters. The other method, MNDO, is appropriate for theoretical treatment of carboranes but geometries are less well reproducible. This is evident from the 90^{o} dihedral angle calculated for biphenyl, while AM1 gives a more reasonable value of about 50^{o}.

Analysis of results in Table 6 (except for PhNCS) shows that the HF method overestimates the solution dipole moments and calculated values are closer to experimental gas phase dipole moments.[9] In contrast, the DFT methods underestimate the solution dipole moments. A comparison of the experimental and computed values also shows a better correlation for the HF method than for the DFT.

Phenyl isothiocyanate (PhNCS) is the most difficult to calculate presumably due to the presence of the sulfur atom. AM1 significantly underestimates the value of the solution dipole moment, while HF overestimates it by about 40%. This variation in computed dipole moments correlates with the values for the calculated C-N-C angle: the smallest angle (138 ^{o}) is obtained at the AM1 level, intermediate at the DFT level (153 ^{o}), and 180 ^{o} using the HF method. This large variation in both geometry and polar properties, renders all these methods unreliable for theoretical treatment of 6-CHBT.

Table 6. Calculated dipole moments [D] for selected molecular models.

compound	Method				
	AM1	HF/6-31G*	B3LYP/3-21G	B3LYP/6-31G*	Experimental
PhOMe	1.25	1.35	1.56	1.31	1.36[a] 1.30 (B)[b]
PhF	1.58	1.68	1.47	1.36	1.61 [c] 1.46 (B) [d]
o-$C_6H_4F_2$	2.68	2.84	2.50	2.28	2.40 (B) [d]
o-FluoroToluene	1.40	1.44	1.18	1.10	1.35 [c] 1.30 (B)[e]
o-Fluoroanisole	2.69	2.77	2.69	2.35	2.31 (B) [f]
PhNCS	2.06	5.13	4.54	3.44	3.62 (B) [g]
2,3-Difluoroanisole	3.98	4.25	4.08	3.60	Na

[a] Gas phase measurement: Groves, L. G.; Sugden, S. *J. Chem. Soc.* 1937, 1782-4. [b] Benzene measurement: Le Févre, C. G.' Le Févre, R. J. W. *J. Chem. Soc.* 1950, 1829-1833. [c] Gas phase measurement: Moore, E. M.; Hobbs, M. E. *J. Am. Chem. Soc.* **1949**, *71*, 411-413. [d] Measured in benzene at 22 °C: Bergmann, E. L.; Engel, L.; Sandor, S. *Z. Physik. Chem*. **1930**, *B10*, 106-120. [e] Benzene measurement: Murty, C. R. *J. Sci. Ind. Research (India)*, **1956**, *15B*, 260. [f] Measured in benzene at 25 °C: Anzilotti, W. F.; Curran, B. C. *J. Am. Chem. Soc.* **1943**, *65*, 607-611. [g] Measured in benzene at 23 °C: Bergmann, E. L.; Engel, L.; Sandor, S. *Z. Physik. Chem*. **1930**, *B10*, 397-413.

Analysis of the data in Table 7 shows that electronic polarizability appears to be systematically underestimated by about 3.0 Å^3 and 3.4 Å^3 with the HF/6-31G(d) and B3LYP/3-21G methods, respectively. The more expensive B3LYP/6-31G(d) method gives more accurate values, which are systematically lower than the experimental by about 2.0 Å^3.

Table 7. Calculated polarizabilities [Å^3] for selected molecular models.

compound	Method				
	AM1	HF/6-31G*	B3LYP/3-21G	B3LYP/6-31G*	Experimental[a]
PhOMe	9.55	9.90	9.89	10.62	13.0
PhF	7.5	7.8	7.4	8.2	10.3
o-$C_6H_4F_2$	7.9	7.8	7.5	8.3	10.4
o-FluoroToluene	8.95	9.42	9.16	9.99	12.3
o-Fluoroanisole	9.9	9.9	9.9	10.7	13.0
PhNCS	14.6	13.9	14.3	15.2	17.3
$B_{12}H_{12}$(-2)	18.5	19.6	19.5	19.9	22.6 [b]
$B_{10}H_{10}$(-2)	15.8	17.3	17.3	17.5	19.3 [c]
2,3-Difluoroanisole	14.6	9.95	10.0	10.8	na

[a] Calculated from n_D and d at 25 ^{o}C using the Lorenz-Lorentz equation without dipole moment contribution. [b] Kaczmarczyk, A.; Kolski, G. B. *Inorg. Chem.* **1965**, *4*, 665. [c] Kaczmarczyk, A.; Kolski, G. B. *J. Phys. Chem.* **1964**, *68*, 1227.

Calculations of mesogens **2**

Molecules **2** were optimized in their most extended conformation. The alkyl groups were in all-trans conformation and set orthogonal to the plane of benzene ring. The alkoxy substituent was coplanar with the benzene ring and anti to the fluorine atoms.

Calculations of the dipole moment components for mesogens **2** show that the smallest values for $\mu_{||}$ are obtained at the AM1 level, moderate at the HF level, and largest using the B3LYP method. At the same time the total dipole moments μ computed at the DFT level are smallest of the three methods. This situation results from relatively large $\mu_{||}$ and small $\mu_{\perp}$ values obtained with the DFT method and gives rise to smallest angles $\beta < 70^{o}$ which are too small to reproduce the extrapolated dielectric permitivities. In contrast, Maier-Meier calculations using either AM1 (*vide infra*) or HF methods allow for reproduction of dielectric properties of **2**. In addition, a plot of longitudinal electric dipole components $\mu_{||}$ vrs σ_p parameters for the rings A show poor correlation for the DFT-derived $\mu_{||}$ ($R^2 = 0.785$), while for the HF values the correlation is excellent ($R^2 = 0.990$). The same correlation of AM1-computed $\mu_{||}$ values is very good ($R^2 = 0.992$) if $\mu_{||}$ for **2B** is excluded. The computed value for **2B** is too small (Table 8), which confirms the inadequacy of the AM1 method for computing boron clusters.

Therefore, dipole moments for analysis with the Maier-Meier equation were obtained using the most reliable HF/6-31G(d) method, and exact electronic polarizabilities were calculated at the B3LYP/3-21G level of theory. The latter are considered to be underestimated by about 10%.

6. Dipole moment and polarizability computational results for 2.

In all these calculations long molecular axes are oriented along the x axes.

Dipole Moments (D) at the HF/6-31G* level of theory (full geometry optimization)

2A X= -1.1379 Y= -3.6265 Z= 0.1582 Tot= 3.8041

2B X= -0.8964 Y= -3.7520 Z= 0.1622 Tot= 3.8610

2C X= -0.5079 Y= -3.8255 Z= 0.3679 Tot= 3.8766

2D X= 0.7096 Y= -3.7397 Z= 0.5561 Tot= 3.8468

Dipole Moments (D) at the B3LYP/6-31G* level of theory (full geometry optimization)

2A X= -1.6776 Y= -2.9778 Z= 0.1017 Tot= 3.4193

2B X= -1.5569 Y= -2.9716 Z= 0.1966 Tot= 3.3605

2C X= -0.8381 Y= -3.2004 Z= 0.2008 Tot= 3.3144

2D X= 1.0460 Y= -3.0852 Z= 0.3998 Tot= 3.2821

Electronic polarizabilities (au) at the B3LYP/3-21G level of theory (full geometry optimization)

2A

Exact polarizability: 611.919 -2.808 300.987 4.787 14.901 243.249

diagonal components: 612.0 304.6 239.6

2B

Exact polarizability: 605.607 -4.932 285.885 4.612 13.519 223.261

diagonal components: 605.74 288.64 220.4

2C

Exact polarizability: 530.947 -1.946 265.396 5.168 13.110 203.655

diagonal components: 531.04 268.07 200.90

2D

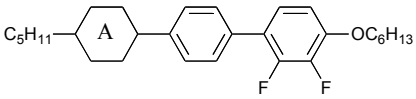
Exact polarizability: 566.787 13.377 228.808 -7.937 23.050 190.291

diagonal components 567.45 239.4 179.1

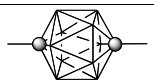
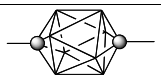
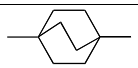
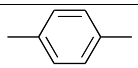
7. Results for computation of molecular and bulk properties of 2 using the AM1 method.

Dipolar and electronic polarizability components obtained with the AM1 method for **2** (Table 8) were used to compute S_{app} and g values using the Maier-Meier equation. The results are shown in Table 9 and the procedure is described in the main text. The values S_{app} and g are smaller that those obtained with the HF/6-31G*-derived molecular parameters but their trends are the same.

Table 8. Calculated (AM1) molecular parameters for **2**.[a]

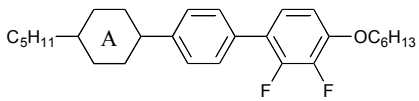


2

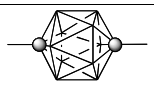
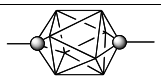
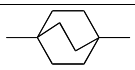
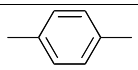
A	**A**	**B**	**C**	**D**
				
$\mu_{\|\|}$ [b] /D	0.61	0.35	0.24	0.42
$\mu_{\perp}$ /D	3.67	3.77	3.85	3.75
μ /D	3.72	3.78	3.85	3.77
β / º	81	85	86	83.5
$\Delta\alpha \times 10^{39}$/ F•m^2	4.23	4.26	3.47	4.59
$\alpha_{avrg} \times 10^{39}$/ F•m^2	5.81	5.51	4.69	4.76

[a] AM1 calculations. [b] The dipole moment vector is orientated from A (negative) to OC_6H_{13} (positive). [b] Angle between the net dipole vector μ and long molecular axes calculated from the vector components.

Table 9. Bulk parameters for **2** calculated using the Maier-Meier equation.[a]



2

A	**A**	**B**	**C**	**D**
				
	g = 0.52±0.05	g = 0.65±0.10	g = 0.73±0.04	g = 0.76±0.10
$\varepsilon_{\|\|}$	1.1±0.2	2.5±0.45	4.2±0.2	4.7±0.5
$\varepsilon_{\perp}$	6.4±0.2	6.8±0.45	6.5±0.2	6.8±0.5
$\Delta\varepsilon$	-5.4	-4.3	-2.3	-2.1
S_{app}	2.7 (2.4–3.2)	1.36 (1.12–1.71)	0.54 (0.51–0.58)	0.51 (0.44-0.62)
For S_{app} = 0.7, g = 1.0				
$\varepsilon_{\perp}$	7.7	8.2	8.5	8.65
$\varepsilon_{\|\|}$	4.4	4.4	4.2	4.6
$\Delta\varepsilon$	-3.3	-3.8	-4.3	-4.1

[a] Molecular parameters from Table 8 (AM1 results) were used.

8. Preparative Details

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 75.4 MHz respectively, on Bruker instruments in $CDCl_3$ and referenced to the solvent, unless specified otherwise. Elemental analysis was provided by Atlantic Microlab, GA.

Optical microscopy and phase identification was performed using a PZO "Biolar" polarized microscope equipped with a HCS250 Instec hot stage. Thermal analysis was obtained using a TA Instruments 2920 DSC. Transition temperatures (onset) and enthalpies were obtained using small samples (2-3 mg) and a heating rate of 5 $^{o}C \bullet min^{-1}$ under a flow of nitrogen gas. The clearing transition was typically less than 0.3 ^{o}C wide.

Suzuki coupling of halides 7 and boronic acid 8. General Procedure for the Preparation of 1-6. Method A.[10] A mixture $Pd(PPh_3)_4$ (0.03 mmol), toluene (5.0 mL), aryl halide **7** (1.0 mmol), and an aqueous solution of Na_2CO_3 (1.0 mL of a 2M solution) under nitrogen atmosphere, and then boronic acid **8** (1.1 mmol) in EtOH (1.0 mL) was added. The mixture was refluxed at a temperature of 110 ^{o}C for approximately 24 hr under vigorous stirring and the progress monitored by TLC analysis (hexane: CH_2Cl_2, 9:1). The reaction mixture was poured into water, the product was extracted with CH_2Cl_2, extracts washed with

brine, and dried (Na_2SO_4). The solution was passed through a silica gel plug, solvent was evaporated and the resulting solid was purified chromatographically on silica gel.

Final purification for analysis was performed as follows: each compound was dissolved in CH_2Cl_2, solution filtered through cotton to remove particles, evaporated and the product recrystallized typically from i-octane occasionally with some toluene and/or EtOH/toluene, and/or MeCN/AcOEt until constant temperature. The resulting crystals were dried in vacuum overnight at ambient temperature. The purity was confirmed by combustion analysis.

Method B. Boronic acid **8** (0.17 mmol), aryl halide **7** (0.14 mmol), and $Pd(AcO)_2$ (1.0 mg) were dissolved in degassed N-methylpyrrolidinone (NMP, 1.5 mL). The flask was flushed with argon and heated to 50 ˚C. Tricyclohexylphosphine (2.0 mg) was added, and the mixture was stirred for 10 minutes. A 2.5 M solution of K_3PO_4 (1.0 mL) was added and the reaction was stirred at 90 ˚C for 8 hr under Ar. The reaction mixture was poured onto water, and the product was extracted into EtOAc. The organic extract was washed with brine and dried (Na_2SO_4). Further purification as described in Method A.

4-Hexyloxy-4'-(12-pentyl-*p*-carboran-1-yl)biphenyl (1A). Obtained from **7A (X=Br)**[11] according to Method A: ^{1}H NMR δ 0.84 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.0 Hz, 3H), 1.00-1.28 (m, 6H), 1.32-1.36 (m, 4H), 1.42-1.48 (m, 2H), 1.5-3.5 (brm, 10H), 1.66 (t, J= 8.3 Hz, 2H), 1.79 (quint, *J* = 7.1 Hz, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H). Anal. Calcd for $C_{25}H_{42}B_{10}O$: C, 64.34; H, 9.07. Found: C, 64.18; H, 9.15.

4-Hexyloxy-4'-(10-pentyl-*p*-carboran-1-yl)biphenyl (1B). Obtained from **7B (X=Br)**[12] according to Method A and crystallized from MeCN. ^{1}H NMR (300 MHz) δ 0.92 (t, *J* = 6.9 Hz, 3H), 0.98 (t, *J* = 7.0 Hz, 3H), 1.34-1.40 (m, 4H), 1.0-3.5 (brm, 8H), 1.42-1.57 (m, 6H), 1.82 (quint, J = 6.9 Hz, 2H), 1.90-2.05 (m, 2H), 3.20 (t, *J* = 8.4 Hz, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H). Anal. Calcd for $C_{25}H_{40}B_8O$: C, 67.77; H, 9.10. Found: C, 67.58; H, 8.84.

4-Hexyloxy-4'-(4-pentylbicyclo[2.2.2]oct-1-yl)biphenyl (1C). Obtained from **7C (X=Br)**[13] according to Method A and recrystallized from EtOH followed by heptane. ^{1}H NMR (300 MHz) δ 0.89 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 6.8 Hz, 3H), 1.11-1.14 (m, 2H), 1.20-1.29 (m, 4H), 1.32-1.38 (m, 6H), 1.42-1.52 (m, 8H), 1.75-1.84 (m, 8H), 3.98 (t, *J* = 6.6 Hz, 2H),

6.94 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 2H). Anal. Calcd for $C_{31}H_{44}O$: C, 86.05; H, 10.25. Found: C, 85.89; H, 10.20.

4-Hexyloxy-4''-pentylterphenyl (1D).[14] Obtained from **7D (X=I)**[15] according to Method A: ^{1}H NMR δ 0.91 (t, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H), 1.35-1.40 (m, 8H), 1.43-1.52 (m, 2H), 1.61-1.68 (m, 2H), 1.81 (quint, J = 6.9 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 4.01 (t, *J* = 6.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.64 and 7.60 (AA'BB', *J* = 8.7 Hz, 4H). Anal. Calcd for $C_{29}H_{36}O$: C, 86.95; H, 9.06. Found: C, 86.54; H, 9.09.

2,3-Difluoro-4-hexyloxy-4'-(12-pentyl-*p*-carboran-1-yl)biphenyl (2A). Obtained from **7A (X=Br)**[11] according to Method B and recrystallized from MeCN, or EtOH/toluene and finally pentane. ^{1}H NMR (300 MHz) δ 0.84 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 6.9, 3H) 1.08-1.26 (m, 6H), 1.32-1.37 (m, 4H), 1.42-1.52 (m, 2H), 1.5-3.5 (brm, 10H), 1.66 (t, J = 8.2 Hz, 2H), 1.83 (quint, J = 7.0 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 6.76 (ddd, J_1 = 9.0 Hz, J_2 = 7.3 Hz, J_3 = 1.7 Hz, 1H), 7.01 (td, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 2H); HRMS calculated for $C_{25}H_{40}B_{10}F_2O$: m/z, 504.3978, found: C, 504.4001.

2,3-Difluoro-4-hexyloxy-4'-(10-pentyl-*p*-carboran-1-yl)biphenyl (2B). Obtained from **7B (X=Br)**[12] according to Method B and recrystallized from MeCN. ^{1}H NMR δ 0.93 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H), 1.0-3.5 (brm, 8H), 1.35-1.40 (m, 4H), 1.44-1.56 (m, 6H), 1.86 (quin, *J* = 7.1 Hz, 2H), 1.95-2.02 (m, 2H), 3.21 (t, *J* = 8.3 Hz, 2H), 4.10 (t, *J* = 6.6 Hz, 2H), 6.83 (ddd, J_1 = 9.0 Hz, J_2 = 7.3 Hz, J_3 = 1.7 Hz, 1H), 7.15 (td, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1H), 7.58 (dd, J_1 = 8.3 Hz, J_2 = 1.5 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H). HRMS calculated for $C_{25}H_{38}B_8F_2O$: 480.3635; found: 480.3639.

2,3-Difluoro-4-hexyloxy-4'-(4-pentylbicyclo[2.2.2]oct-1-yl)biphenyl (2C). Obtained from **7C (X= Br)**[13] according to Method A. ^{1}H NMR δ 0.89 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 6.8 Hz, 3H), 1.12-1.18 (m, 2H), 1.21-1.28 (m, 4H), 1.29-1.38 (m, 6H), 1.47-1.52 (m, 6H), 1.79-1.86 (m, 8H), 4.07 (t, *J* = 6.6 Hz, 2H), 6.78 (ddd, J_1 = 8.9 Hz, J_2 = 7.5 Hz, J_3 = 1.5 Hz, 1H), 7.08 (td, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.43 (brd, *J* = 8.5 Hz, 2H). Anal. Calcd for $C_{31}H_{42}F_2O$: C, 79.45; H, 9.03. Found: C, 79.37; H, 9.08.

2,3-Difluoro-4-hexyloxy-4''-pentylterphenyl (2D).[16] Obtained from **7D (X = Br)**[17] according to Method B and recrystallized from i-octane/toluene. ^{1}H NMR δ 0.91 (t, *J* = 6.8 Hz,

3H), 0.92 (t, J = 7.0 Hz, 3H), 1.34-1.38 (m, 8H), 1.45-1.52 (m, 2H), 1.62-1.71 (m, 2H), 1.87 (quint, J = 7.1 Hz, 2H), 2.65 (t, J = 7.8 Hz, 2H), 4.09 (t, J = 6.6 Hz, 2H), 6.81 (ddd, J_1 = 8.0 Hz, J_2 = 7.2 Hz, J_1 = 1.8 Hz, 1H), 7.14 (td, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1H), 7.27 (d, J = 8.7 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.57 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H). Anal. Calcd for $C_{29}H_{34}F_2O$: C, 79.78; H, 7.85. Found: C, 79.97; H, 7.86.

4-Heptyl-4'-(12-pentyl-p-carboran-1-yl)biphenyl (3A). Obtained from **7A (X=Br)**[11] according to Method B and recrystallized from MeCN and pentane. ^{1}H NMR δ 0.84 (t, J = 7.2 Hz, 3H), 0.89 (t, J = 7.0 Hz, 3H), 1.06-1.33 (m, 12H), 1.5-3.5 (brm, 10H), 1.60-1.68 (m, 4H), 2.62 (t, J = 7.8 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H). Anal. Calcd for $C_{26}H_{44}B_{10}$: C, 67.20; H, 9.54. Found: C, 66.95; H, 9.60.

4-Heptyl-4'-(4-pentylbicyclo[2.2.2]oct-1-yl)biphenyl (3C). Obtained from **7C** (**X = I**) according to Method B and recrystallized from i-octane. ^{1}H NMR δ 0.88 (t, J = 7.2 Hz, 3H), 0.89 (t, J = 7.2 Hz, 3H), 1.10-1.16 (m, 2H), 1.20-1.38 (m, 14H), 1.50 (t, J = 7.8 Hz, 6H), 1.64 (quint, J = 7.3 Hz, 2H), 1.84 (t, J = 7.8 Hz, 6H), 2.63 (t, J = 7.8 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H). Anal. Calcd for $C_{32}H_{46}$: C, 89.24; H, 10.76. Found: C, 89.10; H, 10.81.

4-Heptyl-4''-pentylterphenyl (3D). Obtained from **7D (X = I)**[15] according to Method A and recrystallized from i-octane/toluene. ^{1}H NMR δ 0.89 (t, J = 6.9 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H), 1.27-1.37 (m, 12H), 1.62-1.70 (m, 4H), 2.65 (t, J = 7.7 Hz, 4H), 7.27 (d, J = 8.0 Hz, 4H), 7.56 (d, J = 8.1 Hz, 4H), 7.64 (s, 4H). Anal. Calcd for $C_{30}H_{38}$: C, 90.39; H, 9.61. Found: C, 90.39; H, 9.91.

2,3-Difluoro-4-heptyl-4'-(12-pentyl-p-carboran-1-yl)biphenyl (4A). Obtained from **7A (X=Br)**[11] according to Method A. ^{1}H NMR δ 0.84 (t, J = 6.8 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H), 1.10-1.34 (m, 14H), 1.5-3.5 (brm, 10H), 1.60-1.68 (m, 4H), 2.66 (t, J = 7.6 Hz, 2H), 6.95 (ddd, J_1 = 7.8 Hz, J_2 = 6.7 Hz, J_1 = 1.0 Hz, 1H), 7.01 (td, J_1 = 6.7 Hz, J_2 = 1.4 Hz, 1H), 7.27 (d, J = 8.6 Hz, 2H), 7.33 (dd, J_1 = 8.6 Hz, J_2 = 1.4 Hz, 2H). Anal. Calcd for $C_{26}H_{42}B_{10}F_2$: C, 62.32; H, 8.45. Found: C, 62.57; H, 8.48.

2,3-Difluoro-4-heptyl-4'-(4-pentylbicyclo[2.2.2]oct-1-yl)biphenyl (4C). Obtained from **7C (X= I)** according to Method B and recrystallized from hexane followed by

MeCN/AcOEt. ^{1}H NMR δ 0.886 (t, J = 6.8 Hz, 3H), 0.892 (t, J = 7.1 Hz, 3H), 1.11-1.14 (m, 2H), 1.21-1.37 (m, 14H), 1.50 (t, J = 7.9 Hz, 6H), 1.58-1.66 (m, 2H), 1.84 (t, J = 7.9 Hz, 6H), 2.67 (t, J = 7.8 Hz, 2H), 6.93-6.98 (m, 1H), 7.09 (td, J_1 = 7.5 Hz, J_2 = 1.6 Hz, 1H), 7.39 (d, J = 8.6 Hz, 2H), 7.46 (dd, J_1 = 8.4 Hz, J_2 = 1.4 Hz, 2H). Anal. Calcd for $C_{32}H_{44}F_2$: C, 82.36; H, 9.50. Found: C, 82.36; H, 9.49.

2,3-Difluoro-4-heptyl-4''-pentylterphenyl (4D).[16] Obtained from **7D (X =I)**[15] according to Method A and recrystallized from i-octane/toluene. ^{1}H NMR δ 0.89 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 6.9 Hz, 3H), 1.25-1.40 (m, 12H), 1.62-1.72 (m, 4H), 2.65 (t, J = 7.9 Hz, 2H), 2.70 (t, J = 7.6 Hz, 2H), 7.00 (brt, J = 6.9 Hz, 1H), 7.15 (td, J_1 = 7.5 Hz, J_2 = 1.6 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.60 (dd, J_1 = 8.2 Hz, J_2 = 1.1 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H).

4-Ocyloxy-4'-(10-pentyl-*p*-carboran-1-yl)biphenyl (5B). Obtained from **7B (X=Br)**[12] according to Method B and purified chromatographically (SiO_2, hexanes) followed by repeated recrystallization from EtOH/toluene followed by MeCN/AcOEt and finally from pentane: ^{1}H NMR δ 0.8-3.5 (brm, 8H), 0.90 (t, J = 6.8 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H), 1.25-1.54 (m, 16H), 1.82 (quint, J = 7.0 Hz, 2H), 1.93-2.02 (m, 2H), 3.20 (t, J = 8.3 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 7.57 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz) δ 14.1, 14.2, 22.5, 22.7, 26.1, 29.3, 29.4 (2C), 31.6, 31.8 (2C), 34.5, 68.1, 114.8, 116.4 and 120.4 (carborane), 126.5, 128.1, 129.3, 132.8, 136.7, 141.1, 158.9; ^{11}B NMR (128 MHz) δ -12.0 (d, J = 146 Hz); IR 2596 (B-H) cm^{-1}. Anal. Calcd for $C_{27}H_{44}B_8O$: C, 68.83; H, 9.41. Found: C, 69.03; H, 9.47.

2,3-Difluoro-4-octyloxy-4'-(12-pentyl-p-carboran-1-yl)biphenyl (6A). Obtained from **7A (X=Br)**[11] according to Method B and recrystallized from MeCN/AcOEt and finally from pentane. ^{1}H NMR (300 MHz) δ 0.84 (t, J = 7.3 Hz, 3H), 0.86 (t, J = 6.8, 3H) 1.08-1.37 (m, 10H), 1.42-1.50 (m, 2H), 1.5-3.5 (brm, 10H), 1.66 (t, J = 8.2 Hz, 2H), 1.83 (quint, J = 7.1 Hz, 2H), 4.05 (t, J = 6.6 Hz, 2H), 6.76 (ddd, J_1 = 9.0 Hz, J_2 = 7.2 Hz, J_3 = 1.8 Hz, 1H), 7.01 (td, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1H), 7.25 (d, J = 8.8 Hz, 2H), 7.30 (dd, J_1 = 8.8 Hz, J_2 = 1.2 Hz, 2H); ^{11}B NMR (64 MHz) δ -12.4 (d, J = 164 Hz). Anal. Calcd for $C_{27}H_{44}B_{10}F_2O$: C, 61.10; H, 8.36. Found: C, 61.23; H, 8.53.

2,3-Difluoro-4-octyloxy-4'-(10-pentyl-*p*-carboran-1-yl)biphenyl (6B). Obtained from **7B (X=Br)** [12] according to Method B, isolated chromatographically (SiO_2, hexane), and repeatedly recrystallized from MeCN/AcOEt and finally from pentane. ^{1}H NMR (300 MHz) δ 0.89 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.0 Hz, 3H), 1.0-3.5 (brm, 8H), 1.20-1.60 (m, 14H), 1.86 (quin, *J* = 7.3 Hz, 2H), 1.95-2.02 (m, 2H), 3.21 (t, *J* = 8.3 Hz, 2H), 4.10 (t, *J* = 6.6 Hz, 2H), 6.83 (ddd, J_1 = 9.0 Hz, J_2 = 7.3 Hz, J_3 = 1.7 Hz, 1H), 7.15 (td, J_1 = 8.5 Hz, J_2 = 2.3 Hz, 1H), 7.58 (dd, J_1 = 8.3 Hz, J_2 = 1.5 Hz, 2H), 7.85 (d, *J* = 8.3 Hz, 2H). HRMS calculated for $C_{27}H_{42}B_8F_2O$: 508.3948; found: 508.3969.

2,3-Difluoro-4-octyloxy-4'-(4-pentylbicyclo[2.2.2]oct-1-yl)biphenyl (6C). Obtained from **7C** (**X= I)** according to Method B and recrystallized from heptane. ^{1}H NMR (300 MHz) δ 0.91 (t, *J* = 6.9 Hz, 6H), 1.12-1.18 (m, 2H), 1.21-1.38 (m, 14H), 1.47-1.52 (m, 6H), 1.79-1.86 (m, 8H), 4.07 (t, *J* = 6.6 Hz, 2H), 6.79 (brt, J = 8.6 Hz, 1H), 7.08 (td, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.44 (brd, *J* = 8.7 Hz, 2H). Anal. Calcd for $C_{31}H_{42}F_2O$: C, 79.79; H, 9.33. Found: C, 79.59; H, 9.34.

1-(4-Bromophenyl)-4-pentylbicyclo[2.2.2]octane (7C, Hal = Br).[13] It was obtained by alkylation of bromobenzene according to a literature procedure:[13] ^{1}H NMR δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.08–1.14 (m, 2H), 1.18-1.38 (m, 6H), 1.47 (t, *J* = 7.8 Hz, 6 H), 1.76 (t, *J* = 7.8 Hz, 6H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H).

1-(4-Iodophenyl)-4-pentylbicyclo[2.2.2]octane (7C, Hal = I). Obtained by iodination of 1-phenyl-4-pentylbicyclo[2.2.2]octane[18] according to a general procedure:[19] mp 113 ^{o}C; ^{1}H NMR δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.08–1.14 (m, 2H), 1.18-1.38 (m, 6H), 1.47 (t, *J* = 7.8 Hz, 6H), 1.76 (t, *J* = 7.8 Hz, 6H), 7.06 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H). Anal. Calcd for $C_{24}H_{27}I$: C, 59.69; H, 7.12. Found: C, 59.45; H, 7.23.

4'-Pentyl-4-biphenylyl Triflate (7D, X=OTf). Et_3N (0.17 mL, 1.2 mmol) and triflic anhydride (0.21 mL, 1.2 mmol) were added under argon to a stirred solution of 4'-pentylbiphenyl-4-ol (0.240 g, 1.00 mmol) in CH_2Cl_2 (5 mL) at 0 ^{o}C. The reaction was allowed to warm to room temperature and quenched with water after 3 hr. The product was extracted into CH_2Cl_2, washed with 10% HCl, water, and brine, and dried (Na_2SO_4) Solvent was removed and the resulting yellow oil was passed through a silica gel plug using 1:1 hexane/ CH_2Cl_2. Solvent was removed *in vacuo*, giving 0.364 g (94% yield) of the triflate as a

colorless low melting (about 25 °C) solid: ^{1}H NMR δ 0.91 (t, *J* = 7.0 Hz, 3H), 1.32-1.40 (m, 4H), 1.66 (quint, *J* = 7.5 Hz, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H). It was used for the coupling reaction without further purification.

Areneboronic acids (8). All boronic acids **8** were obtained from appropriate aryl bromides by lithium-halogen exchange with BuLi followed by reaction with $B(OMe)_3$ according to a general literature procedure.[16]

4-Hexyloxyphenylboronic acid (8a).[20] Mp 89-91 °C; ^{1}H NMR (main component) δ 0.93 (t, *J* = 7.0 Hz, 3H), 1.33-1.42 (m, 4H), 1.45-1.55 (m, 2H), 1.78-1.88 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 8.15 (d, *J* = 8.6 Hz, 2H); (minor component ~18%) δ 4.00 (t, *J* = 6.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H). Anal. Calcd for $C_{12}H_{19}BO_3$: C, 64.90; H, 8.62. Found: C, 64.63; H, 8.44.

2,3-Difluoro-4-hexyloxyphenylboronic acid ethylene glycol ester. It was obtained by esterification of the boronic acid **8b**:[16] mp 51-52 °C; ^{1}H NMR δ 0.90 (t, *J* = 7.0 Hz, 3H), 1.29-1.37 (m, 4H), 1.42-1.48 (m, 2H), 1.81 (quint, *J* = 7.1 Hz, 2H), 2.07 (quint, *J* = 5.5 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 4.17 (t, *J* = 5.4 Hz, 4H), 6.69 (ddd, J_1 = 8.4 Hz, J_2 = 6.8 Hz, J_3 = 1.6 Hz, 1H), 7.33 (ddd, J_1 = 8.4 Hz, J_2 = 6.4 Hz, J_3 = 2.4 Hz, 1H). Anal. Calcd for $C_{14}H_{19}BF_2O_2$: C, 59.19; H, 6.74. Found: C, 60.05; H, 7.09.

4-Heptylphenylboronic acid (8c).[21] Recrystallized from pentane: mp 50-70 °C; ^{1}H NMR (main component) δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.25-1.35 (m, 8H), 1.75-1.85 (m, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 8.15 (d, *J* = 8.0 Hz, 2H); (minor component ~17%) 2.64 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H). Anal. Calcd for $C_{13}H_{21}BO_2$: C, 70.94; H, 9.62. Found: C, 69.15; H, 8.78.

2,3-Difluoro-4-heptylphenylboronic acid (8d).[16] Mp 64-67 °C; ^{1}H NMR δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.24-1.39 (m, 8H), 1.60-1.68 (m, 2H), 2.73 (t, *J* = 7.1 Hz, 2H), 7.00 (brt, *J* = 6.9 Hz, 1H), 7.46 (ddd, J_1 = 7.7 Hz, J_2 = 6.0 Hz, J_3 = 1.6 Hz, 1H). Anal. Calcd for $C_{13}H_{19}BF_2O_2$: C, 60.97; H, 7.48. Found: C, 60.69; H, 7.63.

2,3-Difluoro-4-octyloxyphenylboronic acid (8f).[16] Recrystallized from toluene: mp 98-105 °C; ^{1}H NMR (main component) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.25-1.38 (m, 8H), 1.42-1.52 (m, 2H), 1.83 (quint, *J* = 7.4 Hz, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 4.92 (d, *J* = 5.7 Hz, 2H), 6.78

(ddd, J_1 = 8.3 Hz, J_2 = 7.1 Hz, J_3 = 1.2 Hz, 1H), 7.48 (ddd, J_1 = 8.8 Hz, J_2 = 6.6 Hz, J_3 = 2.2 Hz, 1H). Anal. Calcd for $C_{14}H_{21}BF_2O_3$: C, 58.77; H, 7.40. Found: C, 58.61; H, 7.56.

1-Bromo-4-heptylbenzene (9).[16] Following an analogous literature procedure,[20] a solution of 1-bromoheptane (18.8 mL, 120 mmol) in diethyl ether (20 mL) was added dropwise to a stirred suspension of ground Mg (3.0 g) in diethyl ether (25 mL) under argon at a rate to maintain reflux. The mixture was refluxed for 1 hr and the Grignard reagent was added via cannula to a solution of 1,4-dibromobenzene (23.63 g, 100 mmol) and $PdCl_2$(dppf) (0.163 g, 0.20 mmol) in diethyl ether (40 mL) under argon. The reaction mixture was refluxed for 3 hr, then left to stir overnight at room temperature. The reaction was quenched with water and filtered through Celite. The product was extracted into CH_2Cl_2, washed with brine, dried (Na_2SO_4) and concentrated. The resulting orange-red oil was filtered through a silica plug (hexanes). The resulting clear oil was short-path distilled giving 20.63 g (81 % yield) of **9** as a fraction boiling at 80-100 ^oC/0.06 mm Hg (lit.[16] bp 105-115 ^oC/ 0.1 mm Hg): ^1H NMR (300 MHz) δ 0.88 (t, J = 6.8 Hz, 3H), 1.23-1.35 (m, 8H), 1.55-1.62 (m, 2H), 2.55 (t, J = 7.8 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H).

9. Archive files for HF/6-31G(d) calculations

2A

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1\1\GINC-MONSTER\FOpt\RHF\6-31G(d)\C25H40B10F2O1\PIOTR\09-Dec-2005\0\\
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 ,-0.7545415794\C,1.1955321145,0.7066146397,0.9095675977\C,-0.337784210
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2B

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2C

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2D

1\1\GINC-MONSTER\FOpt\RHF\6-31G(d)\C29H34F2O1\PIOTR\03-Dec-2005\0\\#P
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G=C01 [X(C29H34F2O1)]\\@

10. References

(1) S. Urban; J. Kedzierski; R. Dabrowski *Z. Naturforsch.* 2000, **55A**, 449-456.
(2) Urban, S. in Physical Properties of Liquid Crystals: Nematics, D. Dunmur, A. Fukuda, and G. Luckhurst, Eds; IEE, London, 2001, pp 267-276.
(3) Z. Raszewski; R. Dabrowski; Z. Stolarzowa; J. Zmija *Cryst. Res. Technol.* 1987, **22**, 835-844.
(4) D. Dunmur; K. Toriyama In *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: New York, 1998; Vol. 1, p 231-252.
(5) M. Klasen; M. Bremer; A. Götz; A. Manabe; S. Naemura; K. Tarumi *Jpn. J. Appl. Phys.* 1998, **37**, L945-L948.
(6) Gaussian 98, Revision A.7, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
(7) M. J. S. Dewar; C. Jie; E. G. Zoebisch *Organometallics* 1988, **7**, 513.
(8) G. Saitoh; M. Satoh; E. Hasegawa *Mol. Cryst. Liq. Cryst.* 1998, **301**, 13-18.

(9) A. L. McClellan *Table of Experimental Dipole Moments*; Freeman and Co.: San Francisco, 1963.
(10) N. Miyaura; Y. Yanagi; A. Suzuki *Synth. Commun.* 1981, **11**, 513-519.
(11) A. G. Douglass; S. Pakhomov; B. Reeves; Z. Janousek; P. Kaszynski *J. Org. Chem.* 2000, **65**, 1434-1441.
(12) Z. Janousek; P. Kaszynski *Polyhedron,* 1999, **18**, 3517-3526.
(13) G. W. Gray; S. M. Kelly *J. Chem. Soc. Perkin Trans. 2* 1981, 26-31.
(14) G. W. Gray; M. Hird; K. J. Toyne *Mol. Cryst. Liq. Cryst.* 1991, **204**, 43-64.
(15) R. Dabrowski; Z. Witkiewicz; K. Kenig *Mol. Cryst. Liq. Cryst.* 1980, **58**, 251-258.
(16) G. W. Gray; M. Hird; D. Lacey; K. J. Toyne *J. Chem. Soc. Perkin Trans. 2* 1989, 2041-2053.
(17) A. L. Bailey; G. S. Bates *Mol. Cryst. Liq. Cryst.* 1991, **198**, 417-428.
(18) D. K. Girdzhyunaite; P. V. Adomenas *J. Org. Chem. USSR (Engl.Transl.)* 1982, **18**, 707-709.
(19) H. O. Wirth; O. Königstein; W. Kern *Liebigs Ann. Chem.* 1960, **634**, 84-104.
(20) S. Sharma; D. Lacey; P. Wilson *Liq. Cryst.* 2003, **30**, 451-461.
(21) M. R. Friedman; K. J. Toyne; J. W. Goodby; M. Hird *Liq. Cryst.* 2001, **28**, 901-912.