Supplementary material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information for

Symmetric Bent-core Mesogens with *m*-Carborane and Adamantane as the Central Units

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1. Powder XRD for 2[11]

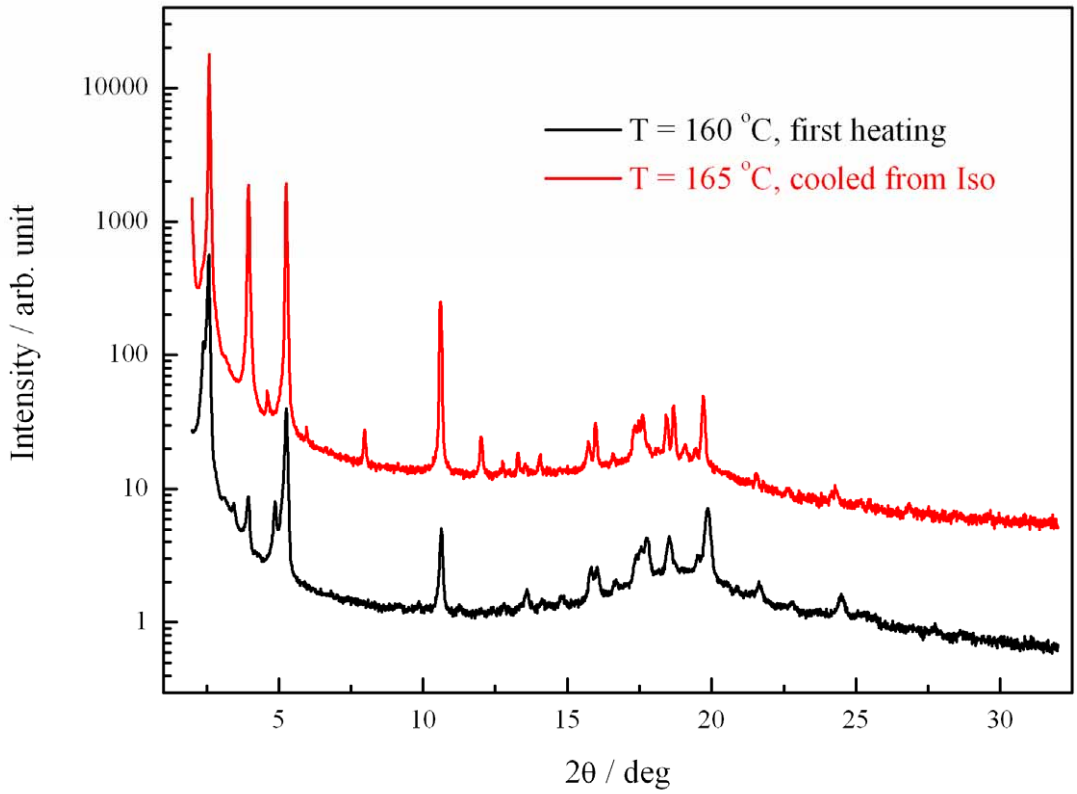


Figure S1. Powder XRD of adamantine derivative **2[11]** obtained on heating of a fresh sample at about 16 K below melting and on cooling from the isotropic phase at about 10 K below melting.

2. Electro-optical response of 1[9]

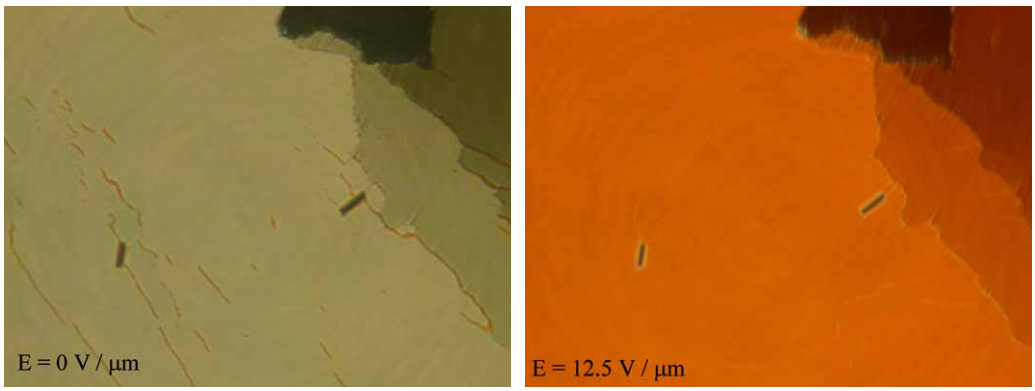
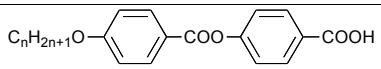
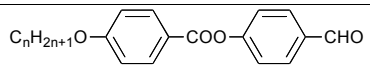


Figure S2. Optical response of **1[9]** to applied electric filed (12.5 V μm^{-1}) measured in a 3.2 µm cell at 155 °C.

3. Transition temperatures for acid and aldehyde intermediates.

Onset transition temperatures were recorded on heating.

Table S1. Transition temperatures (^{o}C) and enthalpies (kJ mol^{-1} in parentheses) determined for **3[n]** and **5[n]** in the heating mode. Cr, crystal; Sm, smectic; I, isotropic.

n	 **3[n]**	 **5[n]**
9	Cr 126 SmC 190 N 229 I (16.5) (2.8) (6.8)	Cr_1 50 Cr_2 56 N 68 I [a] (38.1) (8.4) (0.5)
10	Cr 129 SmC 200 N 226 I (21.6) (3.2) (5.8)	Cr 63 N 70 I [b] (56.1) (0.8)
11	Cr 122 SmC 204 N 222 I (24.4) (4.3) (5.6)	Cr 64 N 71 I (43.1) (0.4)
12	Cr 120 SmC 210 N 222 I [c] (24.8) (4.6) (5.5)	Cr 64 N 76 I (50.7) (1.9)
13	Cr 118 SmC 211 N 218 I (37.2) (6.2) (5.4)	Cr 76 (N 76) I (70.0) (3.2)

[a] Lit: Cr 54 N 66 I. C. Tschierske; H. Zaschke *J. Prakt. Chem.* 1988, **330**, 1-14
[b] Lit: Cr 60 N 69 I. C. Tschierske; H. Zaschke *J. Prakt. Chem.* 1988, **330**, 1-14
[c] Lit: Cr 111-113 N 206 I, S. Greve; V. Vill; W. Friedrichsen *Z. Naturforsch. B,* 2002, **57B**, 677-684

4. Synthetic Details

^{1}H NMR spectra were obtained at 270 or 300 MHz in $CDCl_3$ and referenced to TMS. 13C NMR spectra were obtained at 150.8 MHz in $CDCl_3$. Elemental analysis was provided by Atlantic Microlab, GA. *m*-Carborane was purchased from Katchem s.r.o. (Prague, Czech Republic). Other chemicals were purchased from Aldrich or Tokyo Kasei Ltd.

Preparation of diesters 1[n] and 2[n]. General Procedure. To a suspension of bisphenol **4** (1 eq), carboxylic acid **3[n]** (2.1 eq), and a catalytic amount of DMAP in dry CH_2Cl_2 was added DCC (2.4 eq). The mixture was stirred at room temperature for 8 h, poured into aq. 2 N HCl, and extracted with AcOEt. The organic phase was washed with brine, dried ($MgSO_4$), and then concentrated. CH_2Cl_2 was added to the residue, and the insoluble dicyclohexylurea was filtered. The filtrate was concentrated and the crude ester was purified by column chromatography (SiO_2, 1:1 CH_2Cl_2:*n*-hexane to pure CH_2Cl_2).

The products were repeatedly crystallized from a MeCN/toluene mixture until constant transition temperatures. For DSC and microscopic analysis, each compound was additionally purified by dissolving it in CH_2Cl_2 and filtering to remove particles. The resulting colorless powdery solids were dried in vacuum at ambient temperature.

***m*-Carborane derivatives**

1[9]: ^{1}H NMR δ 0.89 (t, *J* = 6.6 Hz, 6H), 1.28-1.57 (m, 24H), 1.50-3.80 (m, 10H), 1.83 (quint. *J* = 6.6 Hz, 4H), 4.05 (t, *J* = 6.6 Hz, 4H), 6.98 (d, *J* = 8.9 Hz, 4H), 7.15 (d, *J* = 8.9 Hz, 4H), 7.36 (d, *J* = 8.8 Hz, 4H), 7.54 (d, *J* = 8.8 Hz, 4H), 8.15 (d, *J* = 8.9 Hz, 4H), 8.25 (d, *J* = 8.7 Hz, 4H); ^{13}C NMR δ 14.1, 22.7, 26.0, 29.1, 29.3, 29.4, 29.5, 31.8, 68.4,

77.6, 114.4, 120.9, 121.6, 122.2, 126.5, 129.2, 131.9, 132.4, 132.8, 151.3, 155.6, 163.9, 164.2, 164.3. Anal. Calcd. for $C_{60}H_{72}B_{10}O_{10}$: C, 67.90; H, 6.84. Found: C, 68.12; H, 6.78.

1[10]: ^{1}H NMR δ 0.89 (t, *J* = 6.9 Hz, 6H), 1.28-1.55 (m, 28H), 1.50-3.80 (m, 10H), 1.83 (quint. *J* = 6.8 Hz, 4H), 4.05 (t, *J* = 6.6 Hz, 4H), 6.98 (d, *J* = 8.9 Hz, 4H), 7.15 (d, *J* = 8.7 Hz, 4H), 7.37 (d, *J* = 8.8 Hz, 4H), 7.55 (d, *J* = 8.7 Hz, 4H), 8.15 (d, *J* = 9.1 Hz, 4H), 8.26 (d, *J* = 8.7 Hz, 4H); ^{13}C NMR δ 14.1, 22.7, 26.0, 29.1, 29.3, 29.4, 29.6, 29.6, 31.9, 68.4, 77.6, 114.4, 120.9, 121.6, 122.2, 126.5, 129.2, 131.9, 132.4, 132.8, 151.3, 155.6, 163.9, 164.2, 164.3. Anal. Calcd. for $C_{62}H_{76}B_{10}O_{10}$: C, 68.36; H, 7.03. Found: C, 68.57; H, 7.03.

1[11]: ^{1}H NMR δ 0.89 (t, *J* = 6.8 Hz, 6H), 1.27-1.57 (m, 32H), 1.50-3.80 (m, 10H), 1.83 (quint. *J* = 6.4 Hz, 4H), 4.05 (t, *J* = 6.6 Hz, 4H), 6.98 (d, *J* = 9.0 Hz, 4H), 7.15 (d, *J* = 8.8 Hz, 4H), 7.37 (d, *J* = 8.8 Hz, 4H), 7.55 (d, *J* = 8.8 Hz, 4H), 8.15 (d, *J* = 8.9 Hz, 4H), 8.26 (d, *J* = 8.7 Hz, 4H); ^{13}C NMR δ 14.1, 22.7, 26.0, 29.1, 29.3, 29.4, 29.6, 29.6, 29.6, 31.9, 68.4, 77.6, 114.4, 120.9, 121.6, 122.2, 126.5, 129.1, 131.8, 132.4, 132.8, 151.3, 155.6, 163.9, 164.1, 164.3. Anal. Calcd. for $C_{64}H_{80}B_{10}O_{10}$: C, 68.79; H, 7.22. Found: C, 68.91; H, 7.22.

1[12]: ^{1}H NMR δ 0.88 (t, *J* = 6.9 Hz, 6H), 1.27-1.54 (m, 36H), 1.50-3.80 (m, 10H), 1.83 (quint. *J* = 6.8 Hz, 4H), 4.05 (t, *J* = 6.6 Hz, 4H), 6.98 (d, *J* = 9.0 Hz, 4H), 7.15 (d, *J* = 8.8 Hz, 4H), 7.37 (d, *J* = 8.8 Hz, 4H), 7.55 (d, *J* = 8.8 Hz, 4H), 8.15 (d, *J* = 8.8 Hz, 4H), 8.26 (d, *J* = 8.7 Hz, 4H); ^{13}C NMR δ 14.1, 22.7, 26.0, 29.1, 29.3, 29.4, 29.6, 29.6, 29.6, 29.7, 31.9, 68.4, 77.6, 114.4, 120.9, 121.6, 122.2, 126.5, 129.2, 131.8, 132.4, 132.7,

151.3, 155.5, 163.8, 164.1, 164.3. Anal. Calcd. for $C_{66}H_{84}B_{10}O_{10}$: C, 69.20; H, 7.39. Found: C, 69.34; H, 7.43.

1[13]: ^{1}H NMR δ 0.88 (t, *J* = 6.6 Hz, 6H), 1.22-1.55 (m, 40H), 1.50-3.80 (m, 10H), 1.83 (quint. *J* = 6.5 Hz, 4H), 4.06 (t, *J* = 6.8 Hz, 4H), 6.99 (d, *J* = 8.8 Hz, 4H), 7.15 (d, *J* = 8.6 Hz, 4H), 7.37 (d, *J* = 8.6 Hz, 4H), 7.55 (d, *J* = 8.9 Hz, 4H), 8.15 (d, *J* = 8.7 Hz, 4H), 8.26 (d, *J* = 8.6 Hz, 4H). Anal. Calcd. for $C_{68}H_{88}B_{10}O_{10}$: C, 69.60; H, 7.56. Found: C, 69.69; H, 7.67.

Adamantane derivatives

2[9]: ^{1}H NMR δ 0.89 (t, *J* = 6.8 Hz, 6H), 1.29-1.54 (m, 24H), 1.76-1.89 (m, 6H), 1.99 (s, 8H), 2.08 (s, 2H), 2.35 (s, 2H), 4.05 (t, *J* = 6.6 Hz, 4H), 6.98 (d, *J* = 8.8 Hz, 4H), 7.18 (d, *J* = 8.6 Hz, 4H), 7.36 (d, *J* = 8.9 Hz, 4H), 7.46 (d, *J* = 8.8 Hz, 4H), 8.15 (d, *J* = 8.9 Hz, 4H), 8.27 (d, *J* = 8.7 Hz, 4H). Anal. Calcd. for $C_{68}H_{76}O_{10}$: C, 77.54; H, 7.27. Found: C, 77.56; H, 7.27.

2[10]: ^{1}H NMR δ 0.89 (t, *J* = 7.1 Hz, 6H), 1.20-1.53 (m, 28H), 1.76-1.89 (m, 6H), 1.99 (s, 8H), 2.08 (s, 2H), 2.35 (s, 2H), 4.05 (t, *J* = 6.5 Hz, 4H), 6.99 (d, *J* = 8.7 Hz, 4H), 7.18 (d, *J* = 8.6 Hz, 4H), 7.36 (d, *J* = 8.6 Hz, 4H), 7.47 (d, *J* = 8.6 Hz, 4H), 8.16 (d, *J* = 8.6 Hz, 4H), 8.28 (d, *J* = 8.6 Hz, 4H). Anal. Calcd. for $C_{70}H_{80}O_{10}$: C, 77.75; H, 7.46. Found: C, 77.99; H, 7.32.

2[11]: ^{1}H NMR δ 0.89 (t, *J* = 6.8 Hz, 6H), 1.21-1.53 (m, 32H), 1.76-1.89 (m, 6H), 1.99 (s, 8H), 2.08 (s, 2H), 2.35 (s, 2H), 4.06 (t, *J* = 6.6 Hz, 4H), 6.99 (d, *J* = 8.8 Hz, 4H), 7.19 (d, *J* = 8.7 Hz, 4H), 7.36 (d, *J* = 8.7 Hz, 4H), 7.47 (d, *J* = 8.7 Hz, 4H), 8.16 (d, *J* = 8.8 Hz, 4H), 8.28 (d, *J* = 8.7 Hz, 4H). Anal. Calcd. for $C_{72}H_{84}O_{10}$: C, 77.95; H, 7.63. Found: C, 77.96; H, 7.56.

2[12]: ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 6H), 1.22-1.54 (m, 36H), 1.76-1.89 (m, 6H), 1.99 (s, 8H), 2.08 (s, 2H), 2.36 (s, 2H), 4.05 (t, *J* = 6.4 Hz, 4H), 6.99 (d, *J* = 8.6 Hz, 4H), 7.18 (d, *J* = 8.5 Hz, 4H), 7.36 (d, *J* = 8.5 Hz, 4H), 7.47 (d, *J* = 8.5 Hz, 4H), 8.15 (d, *J* = 8.6 Hz, 4H), 8.28 (d, *J* = 8.5 Hz, 4H). Anal. Calcd. for $C_{74}H_{88}O_{10}$: C, 78.14; H, 7.80. Found: C, 77.86; H, 7.75.

2[13]: ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 6H), 1.22-1.54 (m, 40H), 1.76-1.89 (m, 6H), 1.99 (s, 8H), 2.08 (s, 2H), 2.36 (s, 2H), 4.05 (t, *J* = 6.5 Hz, 4H), 6.99 (d, *J* = 8.8 Hz, 4H), 7.19 (d, *J* = 8.6 Hz, 4H), 7.36 (d, *J* = 8.6 Hz, 4H), 7.47 (d, *J* = 8.7 Hz, 4H), 8.16 (d, *J* = 8.8 Hz, 4H), 8.28 (d, *J* = 8.6 Hz, 4H). Anal. Calcd. for $C_{76}H_{92}O_{10}$: C, 78.32; H, 7.96. Found: C, 78.39; H, 8.03.

Carboxylic acids 3[n]. General procedure. Solid $KMnO_4$ (1.5 mmol) was added to a solution of aldehyde **5[n]** (1 mmol) in acetone (6 mL), and the mixture was stirred at room temperature for 12 h. Aqueous $NaHSO_3$ was added, the mixture was stirred for 1 h, and poured into aqueous 2N HCl. The resulting white precipitate was collected and dissolved in AcOEt. The solution was washed with water and brine, dried ($MgSO_4$), and then concentrated to give the acid **3[n]** in a nearly quantitative yield. Recrystallization from an AcOEt-*n*-hexane mixture gave an analytical sample of acids **3[n]** as a white powder.

3[9]: Mp 127-129 °C; ^{1}H NMR (270 MHz, DMSO) □ 0.85 (t, *J* = 6.9 Hz, 3H), 1.24-1.41 (m, 12H), 1.73 (quint. *J* = 6.4 Hz, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 8.06 (d, *J* = 8.9 Hz, 2H); MS (EI) *m/z* 384 (M^+), 247 (100 %). Anal. Calcd. for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34. Found: C,

71.79; H, 7.61.

3[10]:[1] Mp 126-127 °C; ^{1}H NMR (270 MHz, DMSO) δ 0.84 (t, *J* = 7.0 Hz, 3H), 1.23-1.41 (m, 14H), 1.73 (quint. *J* = 6.6 Hz, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 8.06 (d, *J* = 8.9 Hz, 2H); MS (EI) *m/z* 398 (M^+), 261 (100 %). Anal. Calcd. for $C_{24}H_{30}O_5$: C, 72.34; H, 7.59. Found: C, 72.31; H, 7.73.

3[11]: Mp 120-122 °C; ^{1}H NMR (270 MHz, DMSO) δ 0.87 (t, *J* = 6.8 Hz, 3H), 1.23-1.41 (m, 16H), 1.73 (quint. *J* = 6.6 Hz, 2H), 4.07 (t, *J* = 6.4 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 8.06 (d, *J* = 8.9 Hz, 2H); MS (EI) *m/z* 412 (M^+), 275 (100 %). Anal. Calcd. for $C_{25}H_{32}O_5$: C, 72.79; H, 7.82. Found: C, 72.69; H, 8.03.

3[12]:[1,2] Mp 118-119 °C (lit.[2] mp 111-113 °C); ^{1}H NMR (270 MHz, DMSO) δ 0.84 (t, *J* = 6.6 Hz, 3H), 1.22-1.41 (m, 18 H), 1.73 (quint. *J* = 6.6 Hz, 2H), 4.07 (t, *J* = 6.4 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 8.06 (d, *J* = 8.9 Hz, 2H); MS (EI) *m/z* 426 (M^+), 289 (100 %). Anal. Calcd. for $C_{26}H_{34}O_5$: C, 73.21; H, 8.03. Found: C, 73.12; H, 8.28.

3[13]: Mp 118-119°C; ^{1}H NMR (270 MHz, DMSO) δ 0.84 (t, *J* = 6.6 Hz, 3H), 1.23-1.50 (m, 20H), 1.74 (quint. *J* = 6.6 Hz, 2H), 4.09 (t, *J* = 6.4 Hz, 2H), 7.10 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 8.02 (d, *J* = 8.7 Hz, 2H), 8.07 (d, *J* = 8.7 Hz, 2H), 12.9 (brs, 1H); MS (EI) *m/z* 440 (M^+), 303 (100 %). Anal. Calcd. for $C_{27}H_{36}O_5$: C, 73.60; H, 8.24. Found: C, 73.42; H, 8.28.

1,7-bis(4-Hydroxyphenyl)-*m*-carborane (**4a**). Compound **6a** (2.50 g, 7.0 mmol) was dissolved in CH_2Cl_2 (20 mL), 1M BBr_3/ CH_2Cl_2 solution (8.0 mL) was added

dropwise at 0 ^{o}C, and the mixture stirred at room temperature for 12h. The mixture was purred into ice water and extracted with AcOEt. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated. The product was purified by column chromatography (SiO_2, hexane/AcOEt, 10:1 to 5:1) to give 1,7-bis(4-hydroxyphenyl)-*m*-carborane **(4a)** in 91% yield as colorless needles (AcOEt /hexane): mp 198-199 °C; ^{1}H NMR (CD_3OD) δ 1.50-3.80 (br m, 10H), 6.67 (d, *J* = 8.7 Hz, 4H), 7.28 (d, *J* = 8.9 Hz, 4H). Anal. Calcd. for $C_{14}H_{20}B_{10}O_2$: C, 51.20; H, 6.14. Found: C, 51.14; H, 6.07.

Preparation of Aldehydes 5[n]. General procedure.[3] To a suspension of p-alkoxybenzoic acid (1 eq) and $(COCl)_2$ (1.2 eq.) in dry CH_2Cl_2 was added a drop of DMF, and the mixture was stirred at room temperature. After volatiles were removed, the residue was dissolved in dry CH_2Cl_2, 4-hydroxybenzaldehyde and Et_3N were added, and the mixture was stirred at room temperature overnight. The mixture was poured into aqueous 2N HCl, extracted with CH_2Cl_2, and the extract was washed with water and brine, dried ($MgSO_4$), and then concentrated. The residue was purified by short column chromatography (SiO_2, CH_2Cl_2) giving aldehyde **5[n]** in 90-95% yield as a white powder that was recrystallized from a mixture of CH_2Cl_2 and *n*-hexane.

5[9]:[3] Mp 51-52 °C (lit.[3] mp 54 ^{o}C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.6 Hz, 3H), 1.28-1.55 (m, 12H), 1.83 (quint. *J* = 6.6 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H), 8.14 (d, *J* = 8.6 Hz, 2H), 10.02 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$), δ 14.1, 22.6, 25.9, 29.0, 29.2, 29.3, 29.5, 31.8, 68.3, 114.3, 120.6, 122.4, 131.0, 132.2, 133.7, 155.7, 163.6, 164.0, 190.7; MS (EI) m/z 368 (M^+), 248 (100 %). Anal. Calcd. for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 74.97; H, 7.88.

5[10]:[3] Mp 62.5-63°C (lit.[3] mp 60 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.28-1.60 (m, 14 H), 1.83 (quint. *J* = 6.8 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.7 Hz, 2H), 8.13 (d, *J* = 8.9 Hz, 2H), 10.01 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$), δ 14.2, 22.8, 26.0, 29.13, 29.37, 29.41, 29.6, 32.0, 68.4, 114.4, 120.7, 122.5, 131.1, 132.3, 133.8, 155.8, 163.7, 164.0, 190.7; MS (EI) *m/z* 382 (M^+), 262 (100 %). Anal. Calcd. for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.29; H, 8.22.

5[11]: Mp 64-65°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.27-1.55 (m, 16H), 1.83 (quint. *J* = 6.6 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 6.98 (d, *J* = 9.1 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 8.6 Hz, 2H), 8.14 (d, *J* = 9.1 Hz, 2H), 10.02 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$), δ 14.1, 22.7, 26.0, 29.0, 29.3, 29.51, 29.55, 31.9, 68.3, 114.3, 120.6, 122.4, 131.0, 132.2, 133.7, 155.7, 163.6, 164.0, 190.7; MS (EI) *m/z* 396 (M^+), 276 (100 %). Anal. Calcd. for $C_{25}H_{32}O_4$: C, 75.75; H, 8.13. Found: C, 75.56; H, 8.29.

5[12]:[2] Mp 64-64.5°C (lit.[2] mp 64 °C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.27-1.60 (m, 18H), 1.83 (quint. *J* = 6.8 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 8.6 Hz, 2H), 8.13 (d, *J* = 8.9 Hz, 2H), 10.02 (s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$), δ 14.2, 22.8, 26.1, 29.15, 29.42, 29.63, 29.66, 29.71, 32.0, 68.4, 114.4, 120.7, 122.5, 131.1, 132.3, 133.8, 155.8, 163.7, 164.0, 190.8; MS (EI) *m/z* 410 (M^+), 289 (100 %). Anal. Calcd. for $C_{26}H_{34}O_4$: C, 76.06; H, 8.35. Found: C, 75.90; H, 8.64.

5[13]: Mp 75.5-76°C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.23-1.54 (m, 20H), 1.83 (quint. *J* = 6.4 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 6.98 (d, *J* = 8.8

Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.6 Hz, 2H), 8.14 (d, *J* = 9.1 Hz, 2H), 10.02 (s, 1H); MS (EI) *m/z* 424 (M^+), 303 (100 %). Anal. Calcd. for $C_{27}H_{36}O_4$: C, 76.3; H, 8.55. Found: C, 76.17; H, 8.62.

1,7-bis-(4-Methoxyphenyl)-*m*-carborane (**6a**). *m*-Carborane (3.00 g, 20.8 mmol) was dissolved in DME (50 mL), 1.6 M *n*-butyllithium/hexane solution (27.3 mL, 43.7 mmol) was added dropwise at 0 °C under argon atmosphere. The mixture was stirred at room temperature for 30 min, CuCl (4.3 g, 43.7 mmol) was added in one portion, and the stirring was continued at room temperature for 1.5 h. Pyridine (24.6 mL, 312 mmol) followed by 4-iodoanisole (10.2 g, 43.7 mmol) were added in one portion and the mixture was heated at 100 °C for 40 h. After cooling, the mixture was diluted with Et_2O, stirred at room temperature for 2 h, and filtered through Celite. The filtrate was washed with 10% HCl, $Na_2S_2O_3$ solution, water and brine, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (SiO_2, hexane→hexane/AcOEt, 20:1) to give and 1,7-bis(methoxyphenyl)-*m*-carborane (**6a**) in 65% yield as a white solid: ^{1}H NMR δ 1.50-3.70 (br m, 10H), 3.78 (s, 6H), 6.77 (d, *J* = 9.0 Hz, 4H), 7.37 (d, *J* = 9.0 Hz, 4H).

4. References

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