[closo-1-CB$_{11}$H$_{11}$-1-Ph]$^−$ as a structural element for ionic liquid crystals

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ABSTRACT

Ion pairs **2[Pyr]** and **3[Pyr]** containing [closo-1-CB$_{11}$H$_{11}$-1-Ph]$^−$ as the structural element were synthesized and their liquid crystalline properties were investigated by thermal and optical methods. Their mesogenic behavior was compared to that of the analogous series **1[Pyr]** having a COO linking group between the benzene ring and the cluster, and the observed structure—property relationships are discussed in the context of general trends in related non-ionic liquid crystals.

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1. Introduction

A recently developed method for C-arylation of the [closo-1-CB$_{11}$H$_{12}$]$^−$ cluster [1] has opened up possibilities for synthesis of new materials with improved properties. One such class of materials are ionic liquid crystals (ILC), in which the mesogenic properties are driven by the anisometric anion. These compounds are capable of anisotropic cation transport [2—6] and are of interest for ion batteries [7] and solar cell applications [8]. In this context we have demonstrated that closo-carbaborates [closo-1-CB$_9$H$_{10}$]$^−$ (**A**, Fig. 1) and [closo-1-CB$_{11}$H$_{12}$]$^−$ (**B**) are suitable structural elements for ILC, such as **IA** and **IB** in Fig. 1 [9—11], and ion pairs **1[Pyr]** containing [closo-1-CB$_{11}$H$_{12}$]$^−$ (**B**), exhibit SmA and nematic phases [11]. The new synthetic method [1] opens access to C-aryl derivatives of cluster **B** and enables synthesis of new series of ILC such

as **2[Pyr]** and **3[Pyr]**, including those lacking the ester group and, consequently, with increased chemical stability. The first two members of this new family of ILC, **2c[Pyr]** and **2f[Pyr]**, were reported recently [1].

Here we describe the synthesis and characterization of mesogenic ion pairs **2[Pyr]**, derived from the [closo-1-CB$_{11}$H$_{11}$-1-Ph]$^−$, with the C$_6$H$_{13}$ chain and one derivative **3c[Pyr]** with double length of the alkyl chain. Properties of the new compounds are compared to those of series **1[Pyr]** and are used for structure—property relationship analysis.
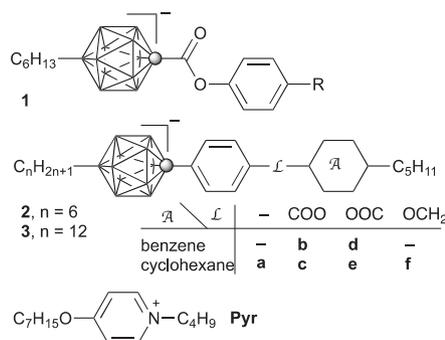
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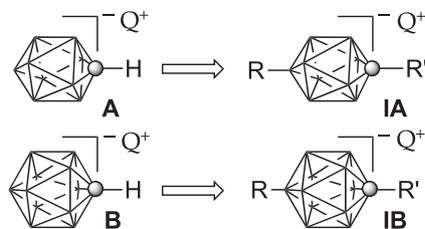
Fig. 1. The structures of the [closo-1-CB$_9$H$_{10}$]$^-$ (**A**) and [closo-1-CB$_{11}$H$_{12}$]$^-$ (**B**) clusters, and ion pairs of their 1,10- (**IA**) and 1,12-disubstituted (**IB**) derivatives with the counterion Q$^+$. Each vertex represents a BH fragment and the sphere is a carbon atom.

2. Results and discussion

2.1. Synthesis

Esters **1b**, **1d**, **2b**, **2c**, and **3c** were prepared from appropriate carboxylic acids **4[NEt$_4$]**–**6[NEt$_4$]**. Thus, carboxylic acids were converted to acid chlorides with (COCl)$_2$ and treated with appropriate phenol **7** or trans-4-pentylcyclohexanol [12] (**8**) to give desired esters as the [NEt$_4$]$^+$ salts (Scheme 1). The reaction with the cyclohexanol was conducted with five-fold excess alcohol, and at high concentration and temperature to assure formation of the esters. Esters **2d[NMe$_4$]** and **2e[NMe$_4$]** were obtained by esterification of phenol **9[NMe$_4$]** with 4-pentylbenzoyl chloride and trans-4-pentylcyclohexanecarbonyl chloride, respectively (Scheme 2). Finally, alkylation of phenol **9[NMe$_4$]** with tosylate **10** [13] in DMF in the presence of K$_2$CO$_3$ resulted in derivative **2f[NMe$_4$]** isolated in 76% yield. The ion pairs **1[Pyr]**–**3[Pyr]** were prepared by exchange of the [NEt$_4$]$^+$ or [NMe$_4$]$^+$ cation for N-butyl-4-heptyloxypyridinium [9,14] (**Pyr**) in a biphasic CH$_2$Cl$_2$/H$_2$O system following the procedure previously reported for the preparation of ion pair **1a[Pyr]** [11].

Carboxylic acid **6[NEt$_4$]** was obtained by Negishi coupling [15,16] of iodo acid [closo-1-CB$_{11}$H$_{10}$-1-(4-C$_6$H$_4$COOH)-12-I]$^-$ [NMe$_4$]$^+$ (**11[NMe$_4$]**) [1] with 12-fold excess dodecylzinc chloride in the presence of Pd(0) and PCy$_3$ ligand generated in-situ (Scheme 3), as described previously for the preparation of acids [closo-1-CB$_{11}$H$_{10}$-1-COOH-12-C$_6$H$_{13}$]$^-$ [NMe$_4$]$^+$ (**4[NMe$_4$]**) [11] and [closo-1-CB$_{11}$H$_{10}$-1-(4-C$_6$H$_4$COOH)-12-C$_6$H$_{13}$]$^-$ [NEt$_4$]$^+$ (**5[NEt$_4$]**) [1]. A similar Negishi coupling of iodo phenol [closo-1-CB$_{11}$H$_{10}$-1-(4-C$_6$H$_4$OH)-12-I]$^-$ [NMe$_4$]$^+$ (**12[NMe$_4$]**) gave the hexyl phenol **9[NMe$_4$]** [1].

Preparation of iodo acid **11[NMe$_4$]** and iodo phenol **12[NMe$_4$]** is described elsewhere [1] and involves arylation of [closo-1-CB$_{11}$H$_{11}$-12-I]$^-$ [NMe$_4$]$^+$ (**13[NMe$_4$]**) with substituted iodobenzene through a carboranylcopper reagent, followed by deprotection of acid or phenol functionality (Scheme 3).

Phenol **7c** (Scheme 1) was obtained according to a literature procedure [17], while synthesis of **7b** was reported before [18].

2.2. Liquid crystalline properties

Transition temperatures for compounds **1[Pyr]** and **2[Pyr]** are shown in Table 1. Phase structures were assigned by comparison of POM results with published textures for reference compounds [19].

Compounds in series **2[Pyr]** and **3c[Pyr]** exhibit a SmA phase identified by the characteristic textures observed in polarized light (Fig. 2a). In ester **2e[Pyr]** and ether **2f[Pyr]** the smectic phase is enantiotropic with a tendency for supercooling (Fig. 3a), while in the remaining esters the SmA phase is monotropic appearing as much as 26 K below melting for ester **2d[Pyr]** (Table 1). Compounds in series **1[Pyr]**, including the newly synthesized phenyl benzoates **1b[Pyr]** and **1d[Pyr]**, exhibit similar phase behavior. Surprisingly, ester **1b[Pyr]** also displays a nematic phase above presumably a SmA phase. The former phase was observed in a supercooled
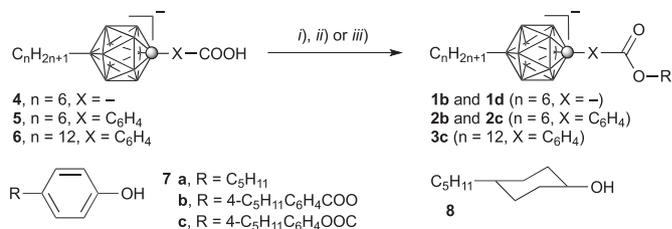
Scheme 1. Reagents and conditions: i) (COCl)$_2$, cat. DMF, CH$_2$Cl$_2$; ii) ROH **7**, Pyr, CH$_2$Cl$_2$, rt; iii) ROH **8**, Pyr, 90 °C, 2 d.
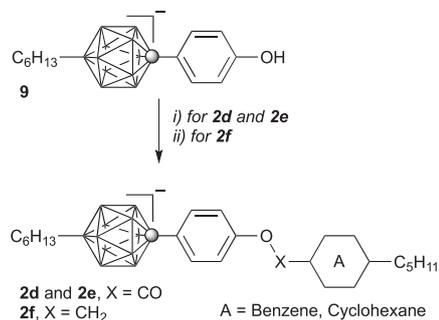
Scheme 2. Reagents and conditions: i) C$_5$H$_{11}$-A-COCl, Pyr, CH$_2$Cl$_2$; ii) C$_5$H$_{11}$-Chx-CH$_2$OTs (**10**), K$_2$CO$_3$, DMF.

microdroplet (Fig. 2b), while the second phase was detected in some DSC scans (Fig. 3b). Nematic phase is rarely observed in ILC and ion pair **1b[Pyr]** represent the second example of a nematic ILC found among boron cluster derivatives [11].

Analysis of data in Table 1 demonstrates that moving the carboxylic group from the {closo-CB$_{11}$} cluster in **1a[Pyr]** to the benzene ring lowers the melting point by 70 K in **2c[Pyr]**. Inversion of the direction of the carboxyl group in **2c[Pyr]** significantly increases stability of the SmA by 47 K in **2e[Pyr]**. In contrast, the same change of the COO group orientation in the benzene analogues **2b[Pyr]** and **2d[Pyr]** and also in **1b[Pyr]** and **1d[Pyr]** results in a much smaller increase of mesophase stability by 8 K and 22 K, respectively.

Replacement of the COO group in **2e[Pyr]** with the CH$_2$O group in **2f[Pyr]** has little effect on the phase stability but significantly lowers the melting point by 31 K.

Compounds with the cyclohexyl ring appear to exhibit more stable SmA phase than their benzene analogues. Thus, replacement of the benzene ring with the cyclohexyl ring moderately increases the SmA-I transition in the pair **2b[Pyr]** and **2c[Pyr]**, while the same replacement in pairs **1d[Pyr]** and **1e[Pyr]**, and **2d[Pyr]** and **2e[Pyr]** stabilizes the SmA phase by 46 K and 57 K, respectively.

A comparison of the clearing temperatures T_c in series **1[Pyr]** and **2[Pyr]** shows that insertion of a COO group between the {closo-1-CB$_{11}$} and Ph groups increases stability of the mesophase by an
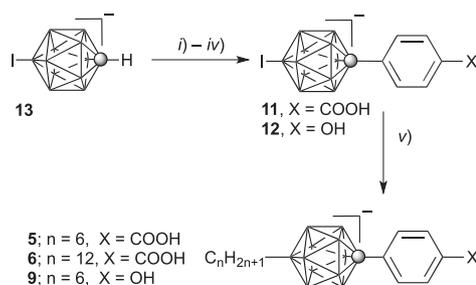
Scheme 3. Reagents and conditions: i) BuLi, THF; ii) CuI; iii) I-C$_6$H$_4$-X', Pd(OAc)$_2$, (o-MeOC$_6$H$_4$)$_3$P; iv) deprotection X' → X; v) C$_n$H$_{2n+1}$ZnCl, Pd$_2$(dba)$_3$, [HPCy$_3$]$^+$[BF$_4$]$^-$, THF.

Table 1
Transition temperatures (°C) and enthalpies (kJ/mol, in parentheses) for **1[Pyr]** and **2[Pyr]**.[a]
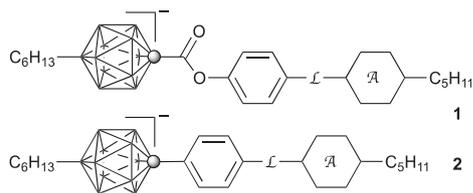
L		A	1[Pyr]	2[Pyr]
—	**a**	Chx	Cr$_1$ 162 Cr$_2$ 178 I[b] (9.8) (24.3)	NA
—COO—	**b**	Ben	Cr 104 (SmX 87 N 93)[c,d] I (64.4) (0.7) (1.7)	Cr 92 (SmA 75)[c] I (59.6) (1.0)
	c	Chx	NA	Cr 108 (SmA 92)[c] I[e] (45.4) (3.9)
—OOC—	**d**	Ben	Cr 125 (SmA 115)[c,f] I (44.7)	Cr 109 (SmA 83)[c] I (72.7) (3.6)
	e	Chx	Cr$_1$ 109 Cr$_2$ 119 SmA 161 I[b] (7.7) (14.9) (6.2)	Cr 136 SmA 139 I (56.9)[g]
—OCH$_2$—	**f**	Chx	NA	Cr 105 SmA 141 I[e] (40.9) (7.7)

[a] Transition temperatures obtained on heating.
[b] Ref. [11].
[c] Monotropic transition.
[d] Obtained on cooling.
[e] Ref. [1].
[f] Optical determination.
[g] Combined enthalpy.

average of 22 K with the smallest effect for the **1b[Pyr]**/**2b[Pyr]** pair (ΔT_c = 18 K) and the largest for the **1d[Pyr]**/**2d[Pyr]** pair (ΔT_c = 32 K).

Increasing the chain length has a desired effect on thermal properties of the ILC: it lowers the melting point by 37 K and increases stability of the SmA phase by 45 K leading to a broad range enantiotropic mesophase (Fig. 4). This change is presumably due to better matching of the length of substituents at the B(12) and C(1) positions of the {closo-CB$_{11}$} cluster and consequently better filling space in head-to-tail molecular arrangement in the SmA phase in **3c** than in **2c**.

Structure–property relationships found in series **1[Pyr]** and **2[Pyr]** are consistent with trends observed for the N–I transition in non-ionic structurally related calamitic mesogens of the general structure **14** (Fig. 5) [20]. Thus, statistical analysis of the difference in T_{NI} for 16 pairs of isostructural mesogenic esters **14a** and **14b**, and four pairs of ethers **14c** shows that replacement of the benzene ring with cylcohexane increases the nematic phase stability by 18 ± 8 K, 20 ± 7 K and 46 ± 2 K, respectively. On the other hand, changing orientation of the ester group from ester of phenol to ester of

cyclohexanol or replacement of the ArOCH$_2$ group with a ArOOC group in cyclohexane derivatives **14d** and **14e**, significantly increases the N phase stability by about 40 K. Similarly, in isostructural analogues of p-carborane **15**, that are closely related to **2d** and **2e**, the cyclohexyl derivative **15a** exhibits higher stability of the nematic phase by 16 K than its benzene analogue **15b** (Fig. 6) [21]. Finally, inserting a COO group between 4-pentylbicyclo[2.2.2]octane group and benzene ring in **14f** increases the mesophase stability by 21 ± 8 K, which is nearly identical to that observed for three pairs **1[Pyr]**/**2[Pyr]**.

3. Summary and conclusions

We have demonstrated that [closo-1-CB$_{11}$H$_{11}$-1-Ph]$^-$ group is a viable structural element of ionic liquid crystals. The removal of the esters linking group between the cluster and the benzene ring in series **1[Pyr]** destabilizes the mesophase by about 20 K, but leads to more chemically stable derivatives, such as **2f[Pyr]** that are resistant to hydrolytic conditions. Increasing the length of the chain has a favorable effect on phase stability and range, which is important for further optimization of properties.

Structure–property relationships observed in series **1[Pyr]** and **2[Pyr]** follow those established for non-ionic liquid crystals, which provides good design tool for new mesogens with desired properties.

4. Experimental section

4.1. General procedures

NMR spectra were obtained at 400 MHz (^{1}H) and 128 MHz (^{11}B) in CD$_3$CN. Chemical shifts were referenced to the solvent (δ ^{1}H, 1.93 ppm) or to an external sample of B(OH)$_3$ in MeOH (δ ^{11}B, 18.1 ppm). Mass spectrometry was acquired in the ESI mode. 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 (0.3–1 mg) and a heating rate of 5 K min^{-1} under a flow of nitrogen gas. For DSC and combustion analyses, each compound was additionally purified by filtering solutions in CH$_2$Cl$_2$ to remove particles, followed by recrystallization from appropriate solvent until constant transition temperatures. The resulting crystals were dried in vacuum at ambient temperature.

4.2. Synthesis of esters 1[NEt$_4$]–3c[NEt$_4$]. General procedure

4.2.1. Method A

[closo-1-CB$_{11}$H$_{10}$-1-COOH-12-C$_6$H$_{13}$]$^-$[NEt$_4$]$^+$ (**4[NEt$_4$]**) [11]. [closo-1-CB$_{11}$H$_{10}$-1-C$_6$H$_4$COOH-12-C$_6$H$_{13}$]$^-$[NEt$_4$]$^+$ (**5[NEt$_4$]**) [1] or
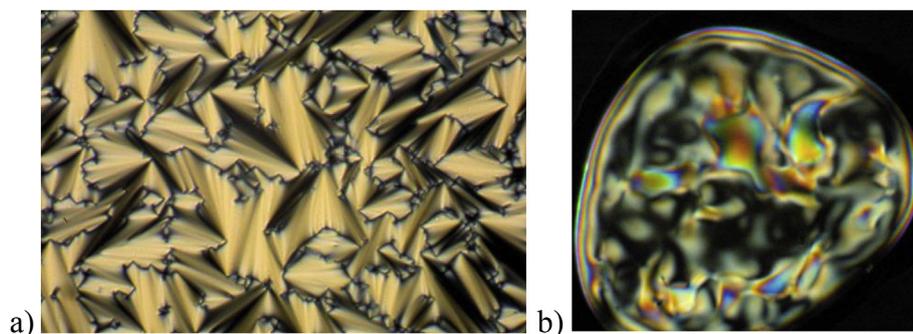

Fig. 2. Optical textures of a SmA phase for **2f[Pyr]** (a) and a nematic phase for **1b[Pyr]** in a supercooled microdroplet (b). Magnification ×50.
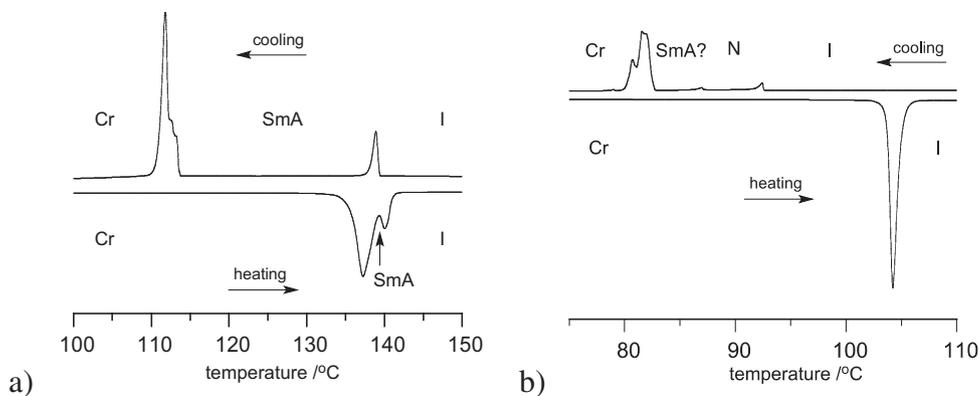
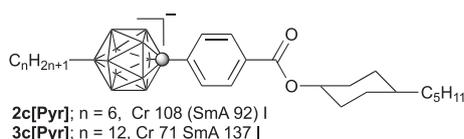**Fig. 3.** DSC trace of ester a) **2e[Pyr]** and b) **1b[Pyr]**; heating rate 5 K min^{-1}.

2c[Pyr]; n = 6, Cr 108 (SmA 92) I
3c[Pyr]; n = 12, Cr 71 SmA 137 I

Fig. 4. A comparison of the transition temperatures for two homologues.

15a, $\mathcal{A}$ = cyclohexane: Cr 101 N 174 I
15b, $\mathcal{A}$ = benzene: Cr 88 N 158 I
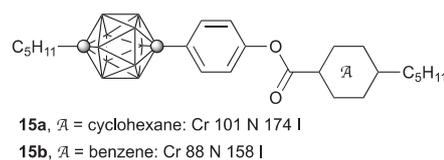
Fig. 6. A comparison of the transition temperatures for two isostructural analogues.

[*closo*-1-CB$_{11}$H$_{10}$-1-C$_6$H$_4$COOH-12-C$_{12}$H$_{25}$]$^-$ [NMe$_4$]$^+$ (**6[NEt$_4$]**) (0.12 mmol) was dissolved in CH$_2$Cl$_2$ (2 mL), oxalyl chloride (COCl)$_2$ (226 mg, 1.78 mmol) and catalytic amounts of DMF were added. The reaction mixture was stirred for 30 min and volatiles were removed *in vacuo*. For the preparation of phenol esters **1b[NEt$_4$]**, **1d [NEt$_4$]**, **2b[NEt$_4$]**, crude acid chloride was dissolved in CH$_2$Cl$_2$ (1 mL), pyridine (24 mg, 0.3 mmol) was added followed by phenol **7** (0.12 mmol) and stirred at ambient temperature overnight. For the preparation of esters **2c[NEt$_4$]** and **3c[NEt$_4$]**, the acid chloride was dissolved in pyridine (48 mg, 0.6 mmol), *trans*-pentylcyclohexanol [12] (102 mg, 0.6 mmol) was added and the reaction mixture was stirred at 90 °C for 2 days followed by removal of volatiles *in vacuo*. The resulting reaction mixture was diluted with CH$_2$Cl$_2$ and washed twice with 10% HCl. The organic layer was separated, and the aqueous layer was extracted (CH$_2$Cl$_2$). Combined CH$_2$Cl$_2$ layers were dried (Na$_2$SO$_4$) and solvent evaporated giving a white crystalline solid of esters as the [NEt$_4$]$^+$ salt. The crude ion pair was passed through a silica gel plug (CH$_2$Cl$_2$/MeCN, 5:1) and used for the subsequent cation exchange.

4.2.2. Method B

4-Pentylbenzoic acid or *trans*-4-pentylcyclohexanecarboxylic acid (0.15 mmol) was dissolved in excess SOCl$_2$ (1 mL), stirred at 75 °C for 2 h and evaporated to dryness *in vacuo*. The resulting crude acid chloride was dissolved in anhydrous CH$_2$Cl$_2$ (2 mL), pyridine (24 mg, 0.30 mmol) and [*closo*-1-CB$_{11}$H$_{10}$-1-C$_6$H$_4$OH-12-
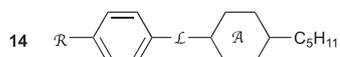
14 $\mathcal{R}$—⬡—$\mathcal{L}$—⬡($\mathcal{A}$)—C$_5$H$_{11}$

a, $\mathcal{L}$ = OOC, $\mathcal{A}$ Chx vrs Ben: ΔT_{NI} = 18±8 K, n = 16
b, $\mathcal{L}$ = COO, $\mathcal{A}$ Chx vrs Ben: ΔT_{NI} = 20±7 K, n = 16
c, $\mathcal{L}$ = OCH$_2$, $\mathcal{A}$ Chx vrs Ben: ΔT_{NI} = 46±2 K, n = 4
d, $\mathcal{A}$ = Chx, $\mathcal{L}$ COO vrs OOC: ΔT_{NI} = 38±5 K, n = 6
e, $\mathcal{A}$ = Chx, $\mathcal{L}$ OOC vrs OCH$_2$: ΔT_{NI} = 41±7 K, n = 12
f, $\mathcal{A}$ = BCO, $\mathcal{L}$ OOC vrs –: ΔT_{NI} = 21±8 K, n =8

Fig. 5. Statistical analysis of difference in T_{NI} for series of n isostructural pairs of mesogens. *Chx* stands for the cyclohexane ring, *Ben* for benzene and *BCO* for bicyclo [2.2.2]octane.

C$_6$H$_{13}$]$^-$ [NMe$_4$]$^+$ (**9[NMe$_4$]**, 50 mg, 0.13 mmol) were added. After stirring overnight, the reaction was worked up and pure esters were isolated as described in Method A.

4.3. Preparation of **1[Pyr]**–**3[Pyr]**. General procedure

The ion pair **1[NEt$_4$]**, **2[NEt$_4$]** or **3[NEt$_4$]** was dissolved in CH$_2$Cl$_2$ and *N*-butyl-4-heptyloxypyridinium bromide [9] (2.0 equiv) was added resulting in formation of a precipitate. Water was added and the biphasic system was stirred vigorously until all the precipitate had dissolved. The CH$_2$Cl$_2$ layer was separated, and the aqueous layer was extracted with additional CH$_2$Cl$_2$. The CH$_2$Cl$_2$ layers were combined, dried (Na$_2$SO$_4$), evaporated and the resulting product was passed through a short silica gel plug (CH$_2$Cl$_2$) giving a white crystalline solid product. Further purification was achieved by repeating recrystallization from EtOH/H$_2$O mixtures (3–5×), and AcOEt/*n*-hexane mixtures (2×) providing pure product as white crystalline material.

4.3.1. Ester **1b[Pyr]**

Obtained in 55% overall yield according to Method A: ^{1}H NMR (400 MHz, CD$_3$CN) δ 0.40–2.50 (m, 10H, B-*H*), 0.47–0.58 (m, 2H, B-C*H$_2$*), 0.88 (t, *J* = 6.7 Hz, 3H, C*H$_3$*), 0.91 (t, *J* = 6.8 Hz, 6H, C*H$_3$*), 0.96 (t, *J* = 7.4 Hz, 3H, C*H$_3$*), 1.13–1.41 (m, 20H, C*H$_2$*), 1.42–1.50 (m, 2H, C*H$_2$*), 1.60–1.68 (m, 2H, C*H$_2$*), 1.77–1.92 (m, 4H, C*H$_2$*), 2.64 (t, *J* = 7.8 Hz, 2H, Benz-C*H$_2$*), 4.29 (t, *J* = 6.7 Hz, 2H, O-C*H$_2$*), 4.31 (t, *J* = 8.1 Hz, 2H, N-C*H$_2$*), 7.13 (d, *J* = 8.5 Hz, 2H, Benz-*H*), 7.19 (d, *J* = 8.7 Hz, 2H, Benz-*H*), 7.28 (d, *J* = 8.5 Hz, 2H, Benz-*H*), 7.34 (d, *J* = 7.4 Hz, 2H, Pyr-*H*), 8.17 (d, *J* = 8.7 Hz, 2H, Benz-*H*), 8.39 (d, *J* = 7.3 Hz, 2H, Pyr-*H*); ^{13}C {^{1}H} NMR (100 MHz, CD$_3$CN) δ 13.8, 14.4, 14.5, 14.6, 20.0, 21.2 (br), 23.2, 23.3, 23.6, 26.3, 29.2, 29.6, 31.2, 31.3, 31.7, 32.2, 32.5, 32.9, 33.6, 33.8, 36.6, 60.6, 72.4, 114.8, 123.3, 123.9, 127.7, 129.8, 131.0, 146.4, 149.6, 149.7, 150.8, 163.8, 166.1, 167.6, 171.7. Anal. Calcd for C$_{42}$H$_{70}$B$_{11}$NO$_5$: C, 64.02; H, 8.95; N, 1.78. Found: C, 64.32; H, 8.95; N, 1.82.

4.3.2. Ester **1d[Pyr]**

Obtained in 56% overall yield according to Method A: ^{1}H NMR (400 MHz, CD$_3$CN) δ 0.40–2.50 (m, 10H, B-*H*), 0.47–0.58 (m, 2H, B-

CH_2), 0.88 (t, $J = 6.3$ Hz, 3H, CH_3), 0.907 (t, $J = 6.1$ Hz, 3H, CH_3), 0.909 (t, $J = 6.0$ Hz, 3H, CH_3), 0.96 (t, $J = 7.4$ Hz, 3H, CH_3), 1.13–1.41 (m, 20H, CH_2), 1.42–1.50 (m, 2H, CH_2), 1.67 (quint, $J = 7.4$ Hz, 2H, CH_2), 1.75–1.92 (m, 4H, CH_2), 2.72 (t, $J = 7.7$ Hz, 2H, Benz-CH_2), 4.29 (t, $J = 6.6$ Hz, 2H, O-CH_2), 4.31 (t, $J = 7.4$ Hz, 2H, N-CH_2), 7.06 (d, $J = 8.9$ Hz, 2H, Benz-H), 7.24 (d, $J = 8.9$ Hz, 2H, Benz-H), 7.34 (d, $J = 7.5$ Hz, 2H, Pyr-H), 7.40 (d, $J = 8.3$ Hz, 2H, Benz-H), 8.08 (d, $J = 8.2$ Hz, 2H, Benz-H), 8.39 (d, $J = 7.5$ Hz, 2H, Pyr-H). Anal. Calcd for $C_{42}H_{70}B_{11}NO_5$: C, 64.02; H, 8.95; N, 1.78. Found: C, 64.20; H, 8.91; N, 1.87.

4.3.3. Ester *2b[Pyr]*

Obtained in 47% overall yield according to Method A: ^{1}H NMR (400 MHz, CD_3CN) δ 0.40–2.50 (m, 10H, B-H), 0.50–0.55 (m, 2H, B-CH_2), 0.88 (t, $J = 6.9$ Hz, 3H, CH_3), 0.91 (t, $J = 6.8$ Hz, 6H, CH_3), 0.96 (t, $J = 7.4$ Hz, 3H, CH_3), 1.15–1.53 (m, 22H, CH_2), 1.64 (quint, $J = 7.5$ Hz, 2H, CH_2), 1.80–1.92 (m, 4H, CH_2), 2.64 (t, $J = 6.6$ Hz, 2H, Benz-CH_2), 4.29 (t, $J = 6.6$ Hz, 2H, O-CH_2), 4.31 (t, $J = 7.5$ Hz, 2H, N-CH_2), 7.11 (d, $J = 8.5$ Hz, 2H, Benz-H), 7.27 (d, $J = 8.4$ Hz, 2H, Benz-H), 7.34 (d, $J = 7.5$ Hz, 2H, Pyr-H), 7.69 (d, $J = 8.6$ Hz, 2H, Benz-H), 7.92 (d, $J = 8.6$ Hz, 2H, Benz-H), 8.39 (d, $J = 7.5$ Hz, 2H, Pyr-H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 13.7, 14.3, 14.4, 14.5, 19.9, 21.0 (br), 23.2, 23.3, 23.5, 26.2, 29.1, 29.5, 31.2, 32.0, 32.2, 32.4, 32.8, 33.5, 33.7, 35.8, 60.5, 72.3, 114.8, 122.5, 122.8, 128.3, 130.3, 132.5, 141.8, 146.4, 149.9, 156.2, 165.4, 167.0, 171.6; ^{11}B{^{1}H} NMR (128 MHz, CD_3CN) δ −13.4 (5B), −11.6 (2B), 3.9 (br, 1B). Anal. Calcd for $C_{41}H_{70}B_{11}NO_3$: C, 66.20; H, 9.48; N, 1.88. Found: C, 66.52; H, 9.42; N, 1.91.

4.3.4. Ester *2d[Pyr]*

Obtained in 62% overall yield according to Method B: ^{1}H NMR (400 MHz, CD_3CN) δ 0.4–2.5 (m, 10H, B-H), 0.45–0.55 (m, 2H, B-CH_2), 0.88 (t, $J = 7.1$ Hz, 3H, CH_3), 0.91 (t, $J = 6.7$ Hz, 3H, CH_3), 0.91 (t, $J = 6.7$ Hz, 3H, CH_3), 0.96 (t, $J = 7.3$ Hz, 3H, CH_3), 1.13–1.53 (m, 22H, CH_2), 1.59–1.68 (m, 2H, CH_2), 1.64 (quint, $J = 7.5$ Hz, 2H, CH_2), 1.86–1.92 (m, 4H, CH_2), 2.64 (t, $J = 7.6$ Hz, 2H, Benz-CH_2), 4.29 (t, $J = 6.6$ Hz, 2H, O-CH_2), 4.31 (t, $J = 7.5$ Hz, 2H, N-CH_2), 7.11 (d, $J = 8.5$ Hz, 2H, Benz-H), 7.27 (d, $J = 8.4$ Hz, 2H, Benz-H), 7.34 (d, $J = 7.5$ Hz, 2H, Pyr-H), 7.69 (d, $J = 8.6$ Hz, 2H, Benz-H), 7.92 (d, $J = 8.6$ Hz, 2H, Benz-H), 8.39 (d, $J = 7.5$ Hz, 2H, Pyr-H); ^{11}B{^{1}H} NMR (128 MHz, CD_3CN) δ −13.4 (5B), −11.6 (5B), 3.9 (br, 1B). Anal. Calcd for $C_{41}H_{70}B_{11}NO_3$: C, 66.20; H, 9.48; N, 1.88. Found: C, 66.42; H, 9.46; N, 1.85.

4.3.5. Ester *2e[Pyr]*

Obtained in 87% overall yield according to Method B: ^{1}H NMR (400 MHz, CD_3CN) δ 0.4–2.5 (m, 10H, B-H), 0.45–0.55 (m, 2H, B-CH_2), 0.87–0.93 (m, 6H, CH_3), 0.88 (t, $J = 6.9$ Hz, 3H, CH_3), 0.96 (t, $J = 7.4$ Hz, 3H, CH_3), 0.98–1.06 (m, 2H, CH_2), 1.12–1.59 (m, 29H, CH and CH_2), 1.80–1.91 (m, 6H, CH_2), 2.09–2.12 (m, 2H, CH_2), 2.46 (tt, $J_1 = 12.2$ Hz, $J_2 = 3.6$ Hz, 1H, CH–COO), 4.29 (t, $J = 6.9$ Hz, 2H, O-CH_2), 4.31 (t, $J = 7.5$ Hz, 2H, N-CH_2), 6.81 (d, $J = 8.8$ Hz, 2H, Benz-H), 7.33 (d, $J = 7.5$ Hz, 2H, Pyr-H), 7.50 (d, $J = 8.8$ Hz, 2H, Benz-H), 8.39 (d, $J = 7.5$ Hz, 2H, Pyr-H); ^{11}B{^{1}H} NMR (128 MHz, CD_3CN) δ −13.3 (5B), −11.7 (5B), 3.4 (1B). Anal. Calcd for $C_{41}H_{76}B_{11}NO_3$: C, 65.66; H, 10.21; N, 1.87. Found: C, 65.77; H, 10.20; N, 1.94.

4.3.6. Ester *3c[Pyr]*

Obtained in 28% overall yield according to Method A: ^{1}H NMR (400 MHz, CD_3CN) δ 0.40–2.50 (m, 10H, B-H), 0.50–0.63 (m, 2H, B-CH_2), 0.86–0.92 (m, 9H, CH_3), 0.96 (t, $J = 7.4$ Hz, 3H, CH_3), 1.00–1.11 (m, 2H, CH_2), 1.13–1.41 (m, 37H, CH and CH_2), 1.42–1.52 (m, 4H, CH_2), 1.78–1.92 (m, 6H, CH_2), 2.00–2.08 (m, 2H, CH_2), 4.29 (t, $J = 6.6$ Hz, 2H, O–CH_2), 4.31 (t, $J = 7.5$ Hz, 2H, N–CH_2), 4.81 (tt, $J_1 = 11.1$ Hz, $J_2 = 4.4$ Hz, 1H, CH–OOC), 7.34 (d, $J = 7.5$ Hz, 2H, Pyr-H), 7.59 (d, $J = 8.6$ Hz, 2H, Benz-H), 7.74 (d, $J = 8.5$ Hz, 2H, Benz-H), 8.39

(d, $J = 7.4$ Hz, 2H, Pyr-H); ^{13}C{^{1}H} NMR (100 MHz, CD_3CN) δ 13.7, 14.36, 14.39, 14.41, 19.9, 23.3, 23.38, 23.40, 26.2, 27.6, 29.1, 29.5, 30.1, 30.39, 30.44, 30.50, 30.56, 31.5, 31.7, 32.39, 32.42, 32.7, 32.9, 33.52, 34.1, 37.3, 37.4, 60.6, 72.3, 74.9, 114.8, 129.2, 129.9, 146.4, 147.7, 166.4, 171.7. Anal. Calcd for $C_{47}H_{88}B_{11}NO_3$: C, 67.68; H, 10.63; N, 1.68. Found: C, 67.96; H, 10.52; N, 1.76.

4.4. *[closo-1-CB$_{11}$H$_{10}$-1-C$_6$H$_4$COOH-12-C$_{12}$H$_{25}$]$^-$ [NEt$_4$]$^+$ (6[NEt$_4$])*

To a solution of anhydrous $ZnCl_2$ (2.10 g, 15.4 mmol) in anhydrous THF (6 mL) under Ar was added $C_{12}H_{25}MgBr$ (14.3 mL, 14.3 mmol, 1.0 M in Et_2O) at 0 °C forming a white, thick slurry, which was stirred for 15 min. Anhydrous NMP (6 mL), $Pd_2(dba)_3$·$CHCl_3$ (24.6 mg, 2 mol %), and, [$HPCy_3$](BF_4) (35.1 mg, 8 mol %) were then added and the reaction mixture turned dark green but slowly faded to red/orange. After 5 min, [*closo*-1-CB$_{11}$H$_{10}$-1-[4-C_6H$_4$COOH]-12-I]$^-$ [NMe$_4$]$^+$ [1] (**11[NMe$_4$]**, 583 mg, 1.18 mmol) was added, and the reaction mixture was stirred at 90 °C until ESI-MS spectrum of a small aliquot (quenched in sat. NH_4Cl and extracted into AcOEt) showed complete conversion to product (about 24 h; if not completed, the palladium source and ligand were further added.). Sat. NH_4Cl (50 mL) was added and the remaining aqueous layer was extracted with Et_2O twice. The organic layers were combined, dried over Na_2SO_4, and solvent was removed giving a black sludge. This material was purified by column chromatography (SiO_2, CH_2Cl_2/CH_3CN 9:1 then CH_2Cl_2/CH_3CN/MeOH 9:3:1). The purity of fractions was confirmed by TLC and ESI-MS analyses. The resulting product was dissolved in AcOEt the solution was washed with 1 N HCl (×2), then with aq. Et_4NBr twice, and dried (Na_2SO_4). The solvent was removed, and the resulting material was dried *in vacuo* giving 426 mg (64% yield) of the 12-dodecyl acid **6[NEt$_4$]** as a pale solid material: ^{1}H NMR (400 MHz, CD_3CN) δ 0.40–2.50 (m, 10H, B-H), 0.48–0.57 (m, 2H, B-CH_2), 0.89 (t, $J = 6.8$ Hz, 3H, CH_3), 1.15–1.35 (m, 32H, CH_2), 3.17 (q, $J = 7.3$ Hz, 8H, CH_2), 7.60 (d, $J = 8.6$ Hz, 2H, Benz-H), 7.76 (d, $J = 8.6$ Hz, 2H, Benz-H); ^{13}C{^{1}H} NMR (124.5 MHz, acetone-d_6) δ 7.7, 14.4, 21.2 (br), 23.3, 29.4, 30.09, 30.16, 30.31, 30.39, 30.46, 30.54, 30.63, 30.68, 32.6, 53.0 (t, $J_{CN} = 3.0$ Hz), 129.2, 129.3, 129.5, 148.3, 167.5; ^{11}B{^{1}H} NMR (128 MHz, CD_3CN) δ −13.3 (5B), −11.6 (5B), 3.4 (br, 1B); ^{11}B{^{1}H} NMR (159 MHz, acetone-d_6) δ −12.9 (5B), −11.1 (5B), 4.0 (1B); EIS-MS, *m/z* 431 (M, 100%). Anal. Calcd for $C_{28}H_{60}B_{11}NO_2$: C, 59.87; H, 10.77; N, 2.49. Found: C, 60.26; H, 10.53; N, 2.39.

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