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Electronic Supplementary Information for

Anion-Driven Mesogenicity: Ionic Liquid Crystals based on the [*closo*-1-CB_9H_{10}]$^-$ Cluster

Bryan Ringstrand,[a] Hirosato Monobe,[b] and Piotr Kaszynski*[a]

[a] *Organic Materials Research Group*, Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA.

[b] *Nanotechnology Research Institute*, National Institute of Advanced Industrial Science and Technology, AIST Kansai Centre, Midorigaoka 1-8-31, Ikeda, Osaka, 536-8577, Japan.

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1. Powder XRD Data

Table S1. X-ray Diffraction Data.

Sample	temp /°C	phase	2θ /°	*d* (exp) /Å	*d* (calcd)	*hkl*	
1d[Pyr]	180	SmA	3.22	27.4	26.6	001	*c* = 26.6 Å
			6.64	13.3	13.3	002	
			10.16	8.7	8.8	003	
			16.5	5.5	halo		
			19.8	4.5	halo		
	140	X	3.09	28.6	27.6	001	*c* = 27.6 Å
			6.40	13.8	13.8	002	
			7.74	11.4			
			9.74	9.1	9.2	003	
			10.78	8.2			
			12.10	7.3			
			13.07	6.8	6.9	004	
			14.31	6.2			
			16.43	5.4	5.5	005	
			17.44	5.1			
			18.03	4.92			
			19.53	4.54			
			19.81	4.48			
2d[Pyr]	140	SmA	3.29	26.8	26.0	001	*c* = 26.0 Å
			6.78	13.0	13.0	002	
			10.29	8.6	8.7	003	
			13.82	6.4	6.5	004	
			16.0	5.5		halo	
			19.9	4.5		halo	
1f[Pyr]	175	SmA	3.32	26.6	25.8	001	*c* = 25.8 Å
			6.85	12.9	12.9	002	
			10.42	8.5	8.6	003	
			16.3-17.1	5.4-5.2		halo	
	155	X_{orth}	3.38	26.1	25.7	001	*a* = 9.0 Å, *b* = 5.2 Å, *c* = 25.7 Å
			6.87	12.9	12.9	002	
			9.83	9.0	9.0	100	
			10.39	8.5	8.6	003, 101	
			13.94	6.4	6.4	004	

		16.98	5.2	5.2	010	
		17.23	5.1	5.1	005, 011	
		19.70	4.50	4.5	110	
		20.00	4.44	4.4	111	
130	X’	3.36	26.3	25.6	001	c = 25. 6 Å
		6.83	12.9	12.8	002	
		7.75	11.4			
		9.77	9.1		100	
		10.31	8.6	8.6	003	
		10.93	8.1			
		12.10	7.3			
		13.80	6.4	6.4	004	
		14.17	6.2			
		14.80	6.0			
		17.35	5.1	5.2	010, 005	
		18.02	4.9			
		19.57	4.53			
		19.89	4.46			

c is calculated from d_{002}.

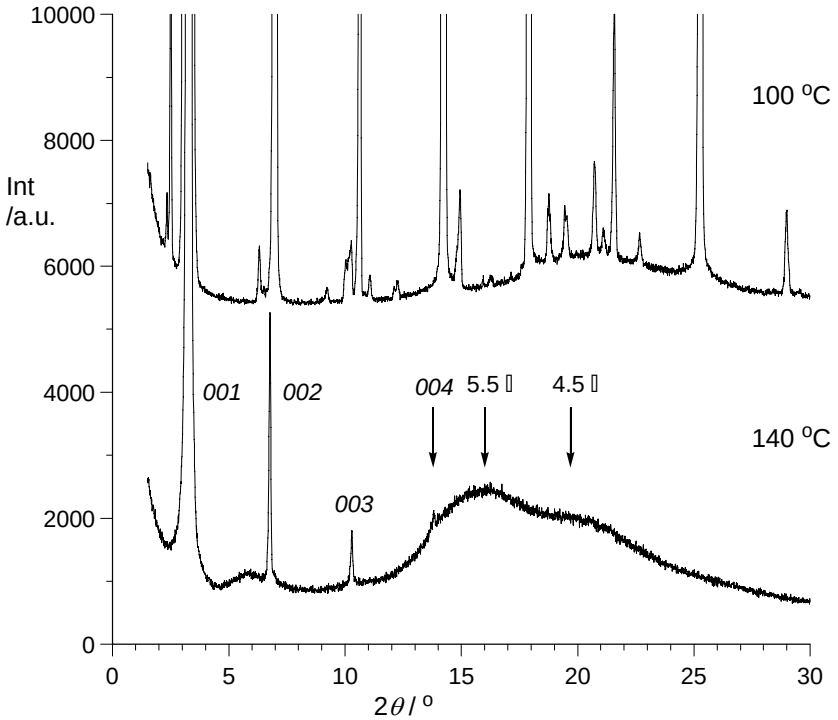


Figure S1. Stacked X-ray diffraction patterns for **2d[Pyr]** at 140 ºC (SmA) and at 100 ºC (crystal phase).

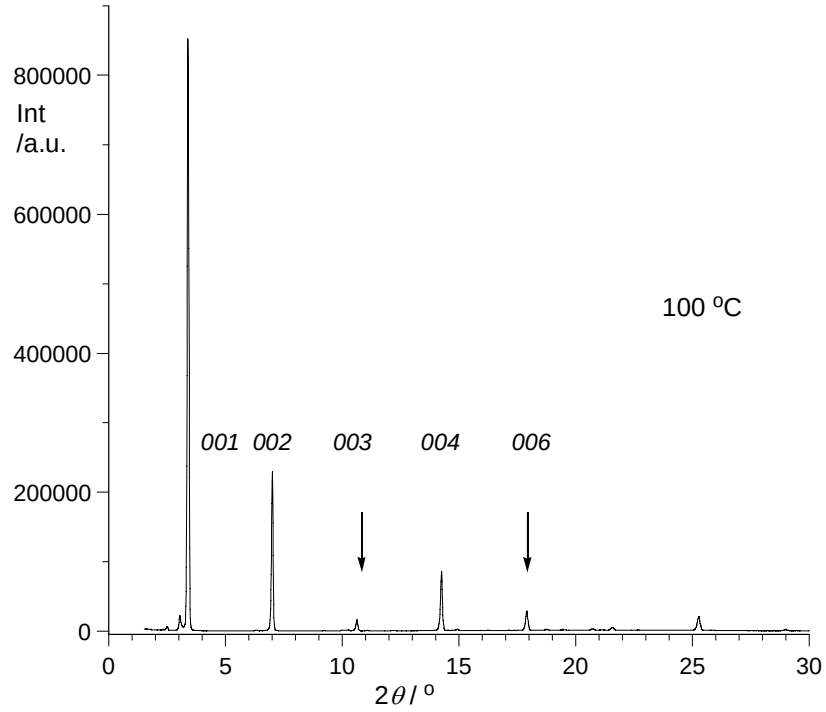


Figure S2. Full scale X-ray diffraction pattern for **2d[Pyr]** at 100 ºC (crystal phase).

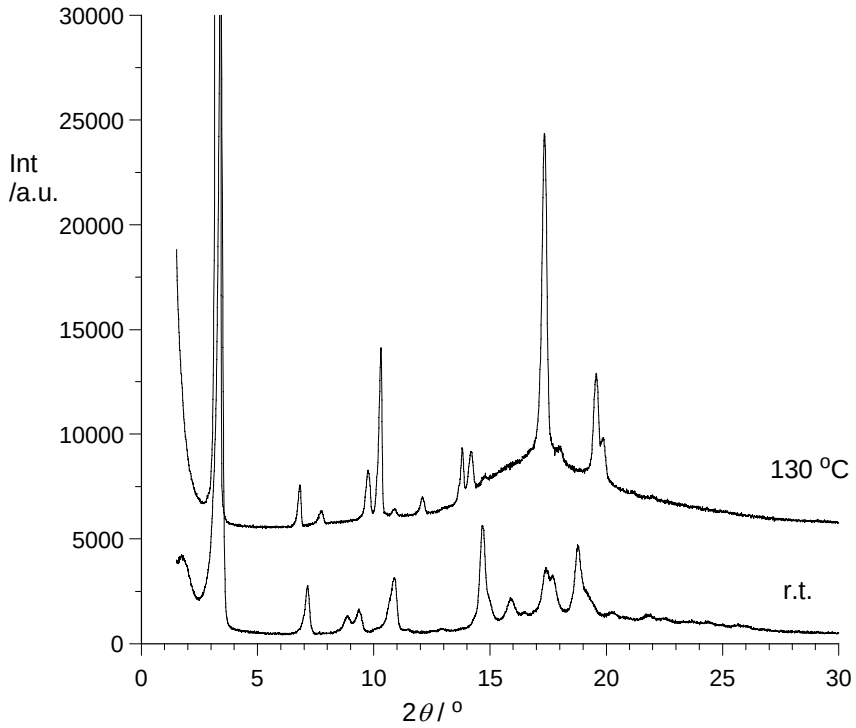
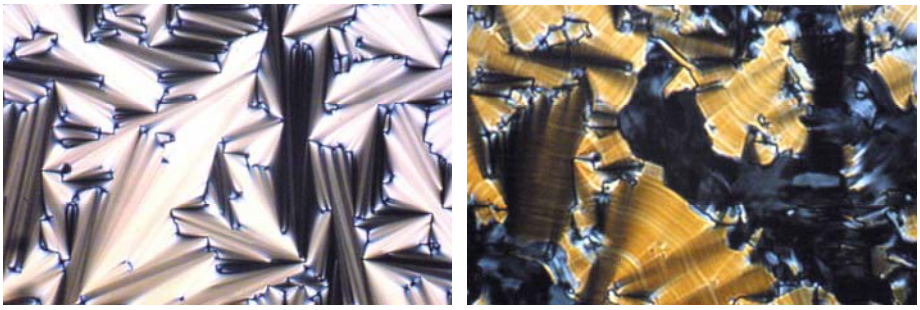


Figure S3. Stacked X-ray diffraction patterns for **1f[Pyr]** at ambient temperature before heating (crystalline phase) and at 130 ºC (phase X).

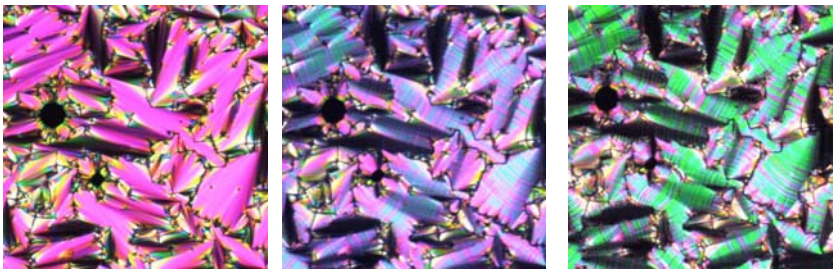
2. Optical textures for selected compounds

Figure S4. Optical textures of an unidentified phase X of **1b[Pyr]** obtained at 106 °C. Magnification ×40.



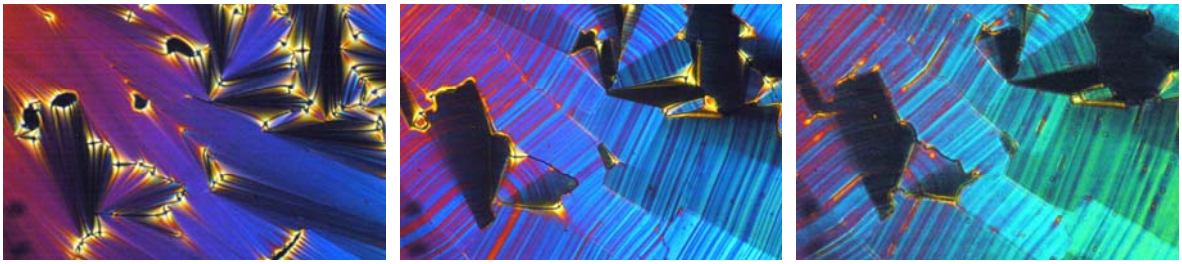
a) b)

Figure S5. Optical textures of **1c[Pyr]** obtained for the same region of the sample upon cooling at (a) SmA at 164 °C (b) unidentified phase X at 91 °C. Magnification ×50.



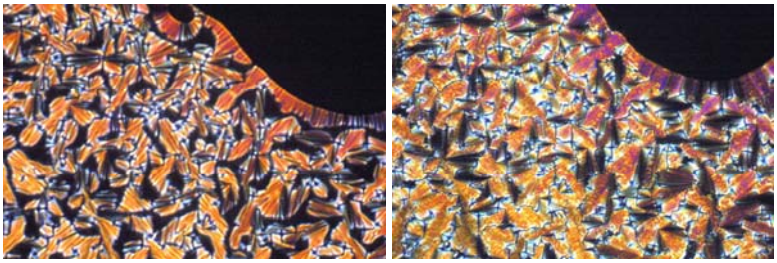
a) b) c)

Figure S6. Optical textures of **1e[Pyr]** obtained for the same region of the sample upon cooling at (a) SmA at 157 °C (b) Phase E at 145 °C (c) Phase X at 120 °C. Magnification ×40.



a) b) c)

Figure S7. Optical textures of **1f[Pyr]** obtained for the same region of the sample upon cooling at (a) SmA at 180 °C (b) Phase E growing from SmA at 167 °C (c) Phase E at 151 °C. Magnification ×50.



a) b)

Figure S8. Optical textures of **2a[Pyr]** obtained for the same region of the sample upon cooling at (a) SmA at 110 °C (b) Phase X at 88 °C. Magnification ×40.

3. Synthetic Details

^{1}H NMR spectra were obtained at 400 MHz field for all compounds, excluding **7**, **1d[NMe$_4$]**, **1e[Pyr]**, and **2c[Pyr]** which were recorded at 300 MHz field, in acetone-d_6 (δ 2.04 ppm), CD_3CN (δ 1.93 ppm) or $CDCl_3$ (δ 7.26 ppm). ^{11}B NMR were recorded at 128 MHz field. Chemical shifts were referenced to the solvent (^{1}H) or to an external sample of $B(OH)_3$ in MeOH (^{11}B, δ = 18.1 ppm). IR spectra were recorded for microcrystalline samples using the ATR technique. Elemental analysis was provided by Atlantic Microlabs.

General Procedure for Preparation of 1[Pyr] and 2[Pyr].

N-Butyl-4-heptyloxypyridinium bromide (**7**, 1.0 equivalent) was added to a solution of ester **1[NMe$_4$]** or diazene **2[NMe$_4$]** or **2[NHEt$_3$]** in CH_2Cl_2 and a precipitate formed. Water was added, and the biphasic system was stirred vigorously until all the precipitate had dissolved. The

CH_2Cl_2 layer was separated, and the aqueous layer was extracted with additional CH_2Cl_2. The CH_2Cl_2 layers were combined, dried (Na_2SO_4), and evaporated giving a white (**1[Pyr]**) or yellow (**2[Pyr]**) crystalline solid, which was recrystallized repeatedly from aqueous alcohol. The resulting crystals were dried in vacuum at ambient temperature.

1a[Pyr]: Recrystallized from EtOH/H_2O mixtures (3x) providing 0.017 g (61% yield for cation exchange) of the pure salt as a white powder: ^{1}H NMR ($CDCl_3$) δ 0.40-2.50 (m, 8H, B-H), 0.86-0.96 (m, 12H), 1.23-1.50 (m, 26H), 1.53-1.60 (m, 2H), 1.75-1.87 (m, 6H), 1.87-1.95 (m, 2H), 1.97-2.04 (m, 2H) 3.96 (t, *J* = 6.5 Hz, 2H), 4.20 (t, *J* = 6.5 Hz, 2H), 4.26 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 8.30 (d, *J* = 7.2 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -24.0 (d, *J* = 139 Hz, 4B), -16.1 (d, *J* = 150 Hz, 4B), 48.2 (s, 1B). Anal. Calcd. for $C_{39}H_{72}B_9NO_4$: C, 64.14; H, 9.66; N, 1.92. Found: C, 64.37; H, 9.78; N, 1.97.

1b[Pyr]: Recrystallized from cold EtOH (3x) providing 0.027 g (24% overall yield based on acid **3[NMe$_4$]**) of the pure salt as a white powder: ^{1}H NMR (acetone-d_6) δ 0.40-2.50 (m, 8H, B-H), 0.83-0.93 (m, 9H), 0.94 (t, *J* = 7.3 Hz, 3H), 1.25-1.50 (m, 24H), 1.56 (quintet, *J* = 7.0 Hz, 2H), 1.73 (quintet, *J* = 7.4 Hz, 2H), 1.83-1.98 (m, 6H), 2.02-2.08 (m, 2H), 2.59 (t, *J* = 7.4 Hz, 2H), 4.45 (t, *J* = 6.5 Hz, 2H), 4.61 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 2H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 2H), 8.89 (d, *J* = 7.4 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -23.9 (d, *J* = 136 Hz, 4B), -16.0 (d, *J* = 148 Hz, 4B), 48.0 (s, 1B). Anal. Calcd. for $C_{39}H_{70}B_9NO_5$: C, 65.39; H, 10.13; N, 1.96. Found: C, 65.19; H, 10.20; N, 2.00.

1c[Pyr]: Recrystallized from EtOH/H_2O mixtures (3x) providing 0.020 g (17% overall yield based on acid **3[NMe$_4$]**) of the pure salt as a white powder: ^{1}H NMR (acetone-d_6) δ 0.40-2.50 (m, 8H, B-H), 0.84-0.92 (m, 9H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.98-1.10 (m, 2H), 1.20-1.44 (m, 21H), 1.45-1.60 (m, 6H), 1.83-1.97 (m, 8H), 2.01-2.08 (m, 2H), 2.10-2.20 (m, 2H), 2.52 (tt, J_1 = 12.2 Hz, J_2 = 3.5 Hz, 1H), 4.46 (t, *J* = 6.5 Hz, 2H), 4.63 (t, *J* = 7.4 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 2H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 2H), 8.90 (d, *J* = 7.5 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -23.9 (d, *J* = 142 Hz, 4B), -16.0 (d, *J* = 147 Hz, 4B), 48.0 (s, 1B). Anal. Calcd. for $C_{42}H_{74}B_9NO_5$: C, 65.48; H, 9.68; N, 1.82. Found: C, 65.47; H, 9.70; N, 1.84.

1d[Pyr]: Recrystallized from EtOH/H_2O mixtures (3x) providing 0.041 g (20% overall yield based on acid **3[NMe$_4$]**) of the pure salt as white crystals: ^{1}H NMR (acetone-d_6) δ 0.40-3.50 (m, 18H, B-H), 0.83 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.91 (t, *J* = 7.6 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H), 1.10-1.43 (m, 18H), 1.45-1.52 (m, 2H), 1.53-1.60 (m, 2H), 1.67-1.75 (m, 2H), 1.83-1.97 (m, 6H), 1.98-2.07 (m, 2H), 4.47 (t, *J* = 6.5 Hz, 2H), 4.64 (t, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 9.0 Hz, 2H), 7.68 (d, *J* = 7.0 Hz, 2H), 8.92 (d, *J* = 6.7 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -23.9 (d, *J* = 132 Hz, 4B), -15.9 (d, *J* = 151 Hz, 4B), -13.2 (d, *J* = 161 Hz, 5B), -12.6 (d, *J* = 154 Hz, 5B), 48.3 (s, 1B). Anal. Calcd. for $C_{38}H_{74}B_{19}NO_5$: C, 54.96; H, 8.98; N, 1.69. Found: C, 55.17; H, 8.99; N, 1.63.

1e[Pyr]: Recrystallized from EtOH/H_2O mixtures (3x) giving 10 mg (20% overall yield based on acid **3[NMe$_4$]**) of the pure salt as white crystals: ^{1}H NMR (300 MHz, acetone-d_6) δ 0.40-2.50 (m, 8H, B-H), 0.84-0.94 (m, 9H), 0.95 (t, *J* = 7.4 Hz, 3H), 1.01-1.20 (m, 2H), 1.21-1.61 (m, 31H), 1.78-2.10 (m, 8H), 2.53 (bt, *J* = 12.2 Hz, 1H), 4.46 (d, *J* = 6.5 Hz, 2H), 4.64 (t, *J* = 7.4

Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 7.5 Hz, 2H), 8.92 (d, *J* = 7.5 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -23.9 (d, *J* = 131 Hz, 4B), -16.1 (d, *J* = 155 Hz, 4B), 48.0 (s, 1B); UV (MeCN), λ_{max} 243 nm, (log ε = 4.32), (CH_2ClCH_2Cl), λ_{max} 248 nm, (log ε = 4.30). Anal. Calcd. for $C_{41}H_{74}B_9NO_3$: C, 67.80; H, 10.27; N, 1.93. Found: C, 68.04; H, 10.33; N, 1.92.

1f[Pyr]: Recrystallized from EtOH/H_2O mixtures (3x) providing 0.030 g (19% overall yield based on acid **3[NMe$_4$]**) of the pure salt as white crystals: ^{1}H NMR (acetone-d_6) δ 0.40-3.50 (m, 18H, B-H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.91 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H), 1.10-1.60 (m, 22H), 1.68-1.76 (m, 2H), 1.82-1.95 (m, 6H), 1.98-2.09 (m, 2H), 4.46 (t, *J* = 6.5 Hz, 2H), 4.64 (d, *J* = 7.4 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 6.2 Hz, 2H), 8.92 (d, *J* = 5.9 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -23.8 (d, *J* = 148 Hz, 4B), -15.9 (d, *J* = 153 Hz, 4B), -12.3 (d, *J* = 157 Hz, 10B) 47.9 (s, 1B). Anal. Calcd. for $C_{37}H_{74}B_{19}NO_3$: C, 56.51; H, 9.48; N, 1.78. Found: C, 56.55; H, 9.51; N, 1.75.

2a[Pyr] as a yellow crystalline solid, which was recrystallized from MeOH (3x) followed by EtOH (3x) giving 0.024 g (32% overall yield based on phenol **5[NMe$_4$]**) of pure **2a[Pyr]** as yellow leaflets: ^{1}H NMR (acetone-d_6) δ 0.40-2.50 (m, 8H, B-H), 0.84-0.89 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H), 1.20-1.62 (m, 28H), 1.77-2.08 (m, 10H), 4.10 (t, *J* = 6.5 Hz, 2H), 4.46 (t, *J* = 6.5 Hz, 2H), 4.63 (t, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 2H), 7.67 (d, *J* = 7.4 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 8.90 (d, *J* = 7.4 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -24.5 (d, *J* = 140 Hz, 4B), -17.1 (d, *J* = 157 Hz, 4B), 42.5 (s, 1B). Anal. Calcd. for $C_{38}H_{72}B_9N_3O_2$: C, 65.17; H, 10.36; N, 6.00. Found: C, 65.45; H, 10.62; N, 6.03.

2b[Pyr]: Recrystallized from MeOH (3x) followed by EtOH (2x) giving 0.052 g (72% overall yield based on phenol **5[NMe$_4$]**) of the pure salt as yellow leaflets: ^{1}H NMR (acetone-d_6) δ 0.40-2.50 (m, 8H, B-H), 0.83-0.91 (m, 6H), 0.92 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H), 1.25-1.51 (m, 24H), 1.58 (quintet, J = 7.1 Hz, 2H), 1.75 (quintet, J = 7.4 Hz, 2H), 1.84-1.94 (m, 6H), 1.96-2.08 (m, 2H), 2.63 (t, J = 7.4 Hz, 2H), 4.45 (t, J = 6.5 Hz, 2H), 4.62 (t, J = 7.4 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 7.4 Hz, 2H), 7.91 (d, J = 8.8 Hz, 2H), 8.90 (d, J = 7.4 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -24.4 (d, J = 136 Hz, 4B), -16.9 (d, J = 149 Hz, 4B), 44.0 (s, 1B). Anal. Calcd. for $C_{38}H_{70}B_9N_3O_3$: C, 63.90; H, 9.88; N, 5.88. Found: C, 64.12; H, 10.03; N, 5.94.

2c[Pyr]: Recrystallized from MeOH (3x) followed by EtOH (2x) giving 0.043 g (38% overall yield based on phenol **5[NMe$_4$]**) of the pure diazene as yellow leaflets: ^{1}H NMR (300 MHz, acetone-d_6) δ 0.40-2.50 (m, 8H, B-H), 0.83-0.93 (m, 9H), 0.94 (t, J = 7.4 Hz, 3H), 0.98-1.13 (m, 2H), 1.20-1.64 (m, 27H), 1.80-2.01 (m, 10H), 2.10-2.22 (m, 2H), 2.55 (tt, J_1 = 12.2 Hz, J_2 = 3.6 Hz, 1H), 4.45 (t, J = 6.5 Hz, 2H), 4.62 (t, J = 7.4 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 7.5 Hz, 2H), 7.91 (d, J = 8.8 Hz, 2H), 8.90 (d, J = 7.5 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -24.4 (d, J = 134 Hz, 4B), -16.9 (d, J = 153 Hz, 4B), 43.6 (s, 1B). Anal. Calcd. for $C_{41}H_{74}B_9N_3O_3$: C, 65.28; H, 9.89; N, 5.57. Found: C, 65.39; H, 9.99; N, 5.57.

2d[Pyr]: Recrystallized from MeOH (3x) followed by EtOH (2x) giving 0.073 g (71% overall yield based on phenol **5[NMe$_4$]**) of pure diazene as yellow needles: ^{1}H NMR (acetone-d_6) δ 0.40-3.50 (m, 18H, B-H), 0.83 (t, J = 7.3 Hz, 3H), 0.85-0.92 (m, 6H), 0.94 (t, J = 7.3 Hz, 3H), 1.08-1.44 (m, 18H), 1.45-1.52 (m, 2H), 1.57 (quintet, J = 7.0 Hz, 2H), 1.67-1.76 (m, 2H), 1.84-

1.93 (m, 6H), 1.95-2.08 (m, 2H), 4.45 (t, *J* = 6.5 Hz, 2H), 4.62 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H), 8.90 (d, *J* = 7.3 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -24.3 (d, *J* = 132 Hz, 4B), -16.7 (d, *J* = 141 Hz, 4B), -13.2 (d, *J* = 153 Hz, 5B), -12.6 (d, *J* = 157 Hz, 5B), 44.0 (s, 1B); UV (MeCN) λ_{max} (log ε), 247 nm (4.41), 305 nm (4.20), 410 nm (2.7). Anal. Calcd. for $C_{37}H_{74}B_{19}N_3O_3$: C, 54.57; H, 9.16; N, 5.16. Found: C, 54.85; H, 9.25; N, 5.16.

General Procedure for Preparation of Esters 1a[NMe$_4$]–1f[NMe$_4$]

Phenol **4** (1.5 equivalents) was added to a colorless solution of [*closo*-1-CB_9H_8-1-COOH-10-C_6H_{13}]$^-$$NMe_4^+$ (**3[NMe$_4$]**, 1.0 equivalent), DCC (1.0 equivalent), and DMAP (0.1 equivalents) in anhydrous CH_2Cl_2. The mixture was stirred overnight at rt, and the reaction progress was monitored by TLC (R_f = 0.5, CH_3CN/CH_2Cl_2, 1:9). The solvent was removed *in vacuo*, and the crude product was isolated by column chromatography (SiO_2, CH_3CN/CH_2Cl_2, 1:9). The resulting ester was washed with hot hexane and recrystallized from EtOH/H_2O or MeOH/H_2O. Esters **1a[NMe$_4$]** and **1b[NMe$_4$]** were difficult to crystallize and were converted directly to *N*-butyl-4-heptyloxypyridinium salts (**1[Pyr]**) without further purification.

1a[NMe$_4$]: The crude product was washed with hot hexane giving 46 mg of ~ 85% pure salt as an oily film that slowly glassified. Attempts to recrystallize from EtOH/H_2O mixtures were unsuccessful: ^{1}H NMR ($CDCl_3$) major signals δ 0.89 (t, *J* = 6.9 Hz, 3H), 0.91 (t, *J* = 6.9 Hz, 3H), 1.56 (quintet, *J* = 6.9 Hz, 2H), 1.78 (quintet, *J* = 7.0 Hz, 2H), 3.01 (s, 12H), 3.94 (t, *J* = 6.5 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H); ^{11}B {^{1}H} NMR (acetone-d_6) δ -24.1 (4B), -16.1 (4B), 48.7 (1B).

1b[NMe$_4$]: The crude product was washed with hot hexane giving 0.053 g of ~ 85% pure salt as a semi-crystalline paste. Attempts to recrystallize from EtOH/H_2O mixtures were unsuccessful: ^{1}H NMR (acetone-d_6) major signals δ 0.88 (t, J = 6.8 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H), 1.73 (quintet, J = 7.4 Hz, 2H), 2.59 (t, J = 7.4 Hz, 2H), 3.43 (s, 12H), 7.20 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 8.9 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -23.9 (d, J = 129 Hz, 4B), -16.0 (d, J = 141 Hz, 4B), 48.0 (s, 1B).

1c[NMe$_4$]: Recrystallized from EtOH/H_2O mixtures (2x) giving 0.020 g (22% yield) of the pure salt as a white crystalline powder: mp 242 °C (DSC); ^{1}H NMR (acetone-d_6) δ 0.40-2.50 (m, 8H, B-H), 0.89 (t, J = 6.9 Hz, 3H), 0.91 (t, J = 7.1 Hz, 3H), 0.95-1.10 (m, 2H), 1.15-1.45 (m, 15H), 1.48-1.62 (m, 4H), 1.80-2.00 (m, 4H), 2.14 (br d, J = 11.2 Hz, 2H), 2.52 (tt, J_1 = 12.2 Hz, J_2 = 3.5 Hz, 1H), 3.43 (s, 12H), 7.18 (d, J = 8.9 Hz, 2H), 7.31 (d, J = 8.9 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -23.9 (d, J = 139 Hz, 4B), -16.0 (d, J = 145 Hz, 4B), 48.9 (s, 1B).

1d[NMe$_4$]: Recrystallized from EtOH/H_2O mixtures (2x) giving 0.041 g (25% yield) of pure salt as a white crystalline powder: mp 226 °C (DSC); ^{1}H NMR (300 MHz, acetone-d_6) δ 0.40-3.50 (m, 18H, B-H), 0.83 (t, J = 7.0 Hz, 3H), 0.91 (t, J = 7.1 Hz, 3H), 1.10-1.30 (m, 6H), 1.34-1.42 (m, 4H), 1.50-1.60 (m, 2H), 1.68-1.75 (m, 2H), 1.81-1.98 (m, 4H), 3.44 (s, 12H), 7.15 (d, J = 9.0 Hz, 2H), 7.33 (d, J = 9.0 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -23.9 (d, J = 137 Hz, 4B), -15.9 (d, J = 152 Hz, 4B), -13.2 (d, J = 160 Hz, 5B), -12.6 (d, J = 158 Hz, 5B), 49.1 (s, 1B).

1e[NMe_4]: The crude product was washed with hot hexane and recrystallized from EtOH/H_2O mixtures (2x) giving 10 mg (26% yield) of the pure salt as a white crystalline powder: mp 197 °C (DSC); ^{1}H NMR (acetone-d_6) δ 0.40-2.50 (m, 8H, B-H), 0.90 (t, *J* = 7.8 Hz, 3H), 0.92 (t, *J* = 7.7 Hz, 3H), 1.05-1.17 (m, 2H), 1.22-1.45 (m, 15H), 1.45-1.62 (m, 4H), 1.85-2.01 (m, 6H), 2.54 (bt, *J* = 12.1 Hz, 1H), 3.45 (s, 12H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -23.9 (d, *J* = 132 Hz, 4B), -16.0 (d, *J* = 152 Hz, 4B), 48.3 (s, 1B).

1f[NMe_4]: Recrystallized from EtOH/H_2O mixtures (2x) giving 0.029 g (23% yield) of the pure salt as a white crystalline powder: mp 201 °C (DSC); ^{1}H NMR (acetone-d_6) δ 0.40-3.50 (m, 18H, B-H), 0.84 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H), 1.10-1.30 (m, 6H), 1.32-1.43 (m, 4H), 1.55 (quintet, *J* = 7.0 Hz, 2H), 1.67-1.75 (m, 2H), 1.80-1.98 (m, 4H), 3.44 (s, 12H) 7.17 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -23.9 (d, *J* = 138 Hz, 4B), -15.9 (d, *J* = 151 Hz, 4B), -12.3 (d, *J* = 164 Hz, 10B), 48.3 (s, 1B).

Preparation of [*closo*-1-CB_9H_8-1-(N=N-C_6H_4-OC_9H_{19}-4)-10-C_6H_{13}]$^-$ NMe_4^+ (2a[NMe_4]).

A solution of 1-bromononane (0.08 mL, 0.4 mmol) in anhydrous CH_3CN (2 mL) was added to an orange solution of azophenol **5[NMe_4]** (0.042 g, 0.106 mmol, about 60% pure; contaminated with NMP) and $NMe_4^+OH^-\cdot 5H_2O$ (0.06 g, 0.32 mmol) in anhydrous CH_3CN (2 mL). The solution was stirred at 50 °C for 4 hr. The reaction mixture was evaporated to dryness, and the crude product was isolated by column chromatography (SiO_2, CH_3CN/CH_2Cl_2, 1:9). Washing with hot hexane gave 0.068 g of crude diazene **2a[NMe_4]** as a yellow/green viscous isotropic film that slowly crystallized. Attempts to recrystallize from MeOH or MeOH/H_2O mixtures were unsuccessful and the product was converted directly to **2a[Pyr]** without further

purification: ^{1}H NMR (acetone-d_6) major signals δ 0.88 (t, *J* = 6.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H), 3.43 (s, 12H), 4.10 (t, *J* = 6.5 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 2H), 7.85 (d, *J* = 8.9 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -24.5 (d, *J* = 138 Hz, 4B), -17.1 (d, *J* = 146 Hz, 4B), 42.8 (s, 1B).

General Procedure for Preparation of Diazenes 2b[NHEt$_3$], 2c[NMe$_4$], and 2d[NHEt$_3$]

A solution of acid chloride **6** (4.0 equivalents) in anhydrous CH_2Cl_2 was added to an orange solution of azophenol **5[NMe$_4$]** (about 60% pure; contaminated with NMP) and NEt_3 (5.0 equivalents) in anhydrous CH_2Cl_2. The bright yellow solution was stirred for 12 hrs, and the reaction progress was monitored by TLC (R_f = 0.5 in CH_3CN/CH_2Cl_2, 1:9). The reaction mixture was worked up and the product was isolated as described for esters **1[NMe$_4$]**. Attempts to recrystallize from MeOH or MeOH/H_2O mixtures were unsuccessful and without crystallization further purification, the resulting diazenes **2b[NHEt$_3$]**, **2c[NMe$_4$]**, or **2d[NHEt$_3$]** were converted to the pyridinium salts **2[Pyr]**.

2b[NHEt$_3$]: Washing with hot hexane gave 0.073 g (135% yield) of crude diazene as a yellow/green viscous isotropic film, which slowly crystallized: ^{1}H NMR (acetone-d_6) major signals δ 0.89 (t, *J* = 6.5 Hz, 3H), 0.92 (t, *J* = 6.9 Hz, 3H), 1.38 (t, *J* = 7.3 Hz, 9H), 1.58 (quintet, *J* = 7.1 Hz, 2H), 1.75 (quintet, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H), 3.42 (q, *J* = 7.3 Hz, 6H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -24.4 (d, *J* = 137 Hz, 4B), -16.9 (d, *J* = 146 Hz, 4B), 43.7 (s, 1B).

2c[NMe$_4$]: Washing with hot hexane gave 0.095 g (110% yield) of crude diazene as a yellow/green viscous isotropic film that slowly crystallized: ^{1}H NMR (acetone-d_6) major signals

δ 0.89 (t, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H), 2.54 (tt, J_1 = 12.2 Hz, J_2 = 3.5 Hz, 1H), 3.43 (s, 12H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.7 Hz, 2H); ^{11}B {^{1}H} NMR (acetone-d_6) δ -24.4 (4B), -16.9 (4B), 43.3 (s, 1B).

2d[NHEt$_3$]: Washing with hot hexane gave 0.087 g (105% yield) of ~ 95% pure diazene as a yellow/green viscous isotropic film that slowly crystallized: mp 155 ^{o}C, ^{1}H NMR (acetone-d_6) δ 0.40-3.50 (m, 18H, B-H), 0.83 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.0 Hz, 3H), 1.06-1.30 (m, 6H), 1.33-1.43 (m, 4H), 1.37 (t, *J* = 7.3 Hz, 9H), 1.52-1.61 (m, 2H), 1.67-1.76 (m, 2H), 1.84-2.00 (m, 4H), 3.39 (q, *J* = 7.3 Hz, 6H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H); ^{11}B NMR (acetone-d_6) δ -24.3 (d, *J* = 137 Hz, 4B), -16.7 (d, *J* = 157 Hz, 4B), -13.2 (d, *J* = 151 Hz, 5B), -12.6 (d, *J* = 158 Hz, 5B), 43.1 (s, 1B).

Preparation of [*closo*-1-CB$_9$H$_8$-1-COOH-10-C$_6$H$_{13}$]$^-$NMe$_4^+$ (3[NMe$_4$])

To a 100 mL three-necked flask, under inert atmosphere, equipped with a magnetic stir bar, reflux condenser, septum, and a glass stopcock was suspended solid anhydrous $ZnCl_2$ (2.29 g, 16.8 mmol) in anhydrous THF (16 mL). $C_6H_{13}MgBr$ in Et_2O (9.2 mL, 16.0 mmol, 1.74 M) was added, and the exothermic reaction was stirred briefly (15 min) producing a white precipitate. Anhydrous NMP (8 mL), Pd_2dba_3 (0.061 g, 0.067 mmol), and $[HPCy_3]^+$ BF_4^- (0.099 g, 0.268 mmol) were added, and the reaction mixture turned dark green and slowly faded to red/orange. After 5 mins, acid[1] [*closo*-1-CB$_9$H$_8$-1-COOH-10-I]$^-$ NMe$_4^+$ (**8[NMe$_4$]**, 0.482 g, 1.33 mmol) was added. The septum was replaced with an additional glass stopcock, and the reaction was stirred at 85°C overnight. After brief heating, the reaction turned from red/orange to black. Sat. NH_4Cl (50 mL) was added, excess THF was removed *in vacuo*, and the remaining aqueous

layer was extracted with Et_2O (3 x 20 mL). The organic layers were combined, dried (Na_2SO_4), and removed giving a black sludge. Excess NMP and 1-hexanol were removed under vacuum (60 °C, 0.5 mm Hg) and the residue (1.13 g) was separated by column chromatography (SiO_2, CH_3CN/CH_2Cl_2, 1:4) giving 0.586 g of [*closo*-1-CB_9H_8-1-COOH-10-C_6H_{13}]$^-H_3O^+$ (**3[H_3O]**) as a yellow/orange oil, which contained remnant NMP by ^{1}H NMR: ^{11}B {^{1}H} NMR (CD_3CN) δ -24.3 (4B), -16.6 (4B), 47.3 (1B).

The crude acid extract was redissolved in 10 % HCl (50 mL) and extracted with Et_2O (3 x 20 mL). The organic layers were combined, and H_2O (10 mL) was added. The Et_2O was removed *in vacuo*, and the aqueous layer was filtered. $NMe_4^+Cl^-$ (0.150 g, 1.37 mmol) was added to the filtrate, and a white precipitate formed, which was filtered, washed (H_2O), and dried *in vacuo* giving 0.383 g (89% yield) of pure **3[NMe_4]**: mp 135 ^{o}C dec; ^{1}H NMR (acetone-d_6) δ 0.40-2.50 (m, 8H, B-H), 0.91 (t, *J* = 7.0 Hz, 3H), 1.35-1.41 (m, 4H), 1.56 (quintet, *J* = 6.9 Hz, 2H), 1.81-1.96 (m, 4H), 3.45 (s, 12H); ^{11}B NMR (acetone-d_6) δ -24.1 (d, *J* = 147 Hz, 4B), -16.5 (d, *J* = 157 Hz, 4B), 46.8 (s, 1B); MS (FAB): *m/z* 244-248 (M-H, max at 247, 100%); FAB-HRMS(-): Calcd. for $C_8H_{22}B_9O_2$ *m/z*: 249.2460; found; 249.2464.

Preparation of [*closo*-1-CB_9H_8-1-(N=N-C_6H_4-OH-4)-10-C_6H_{13}]$^-NMe_4^+$ (5[NMe_4])

To a 100 mL three-necked flask, under inert atmosphere, equipped with a magnetic stir bar, septum, and two glass stopcocks was suspended solid anhydrous $ZnCl_2$ (1.04 g, 7.62 mmol) in anhydrous THF (5 mL). $C_6H_{13}MgBr$ in Et_2O (9.2 mL, 16.0 mmol, 1.74 M) was added, and the exothermic reaction was stirred briefly (15 min) producing a white precipitate. Anhydrous LiCl (0.3 g, 6.93 mmol) dissolved in anhydrous THF (10 mL) was added producing a homogenous solution. Anhydrous NMP (8 mL), Pd_2dba_3 (0.019 g, 0.021 mmol), and $[HPCy_3]^+$

BF_4^- (0.031 g, 0.084 mmol) were added subsequently, and the reaction mixture turned dark green and slowly faded to red/orange. After 5 mins, [*closo*-1-CB_9H_8-1-(N=N-C_6H_4-OH-4)-10-I]$^-NMe_4^+$ (**9[NMe$_4$]**, 0.275 g, 0.63 mmol) was added, and the reaction was stirred at rt overnight. Sat. NH_4Cl (25 mL) was added, THF was removed *in vacuo*, and the remaining aqueous layer was extracted with Et_2O (3 x 20 mL). The organic layers were combined, dried (Na_2SO_4), and solvents removed giving a residue as a black sludge. Excess NMP and 1-hexanol were removed under vacuum (60 °C, 0.5 mm Hg) and the resulting residue (0.740 g) was separated by column chromatography (SiO_2, CH_3CN/CH_2Cl_2, 1:4) giving 0.370 g of (**5[H$_3$O]**) as a yellow/orange film which solidified on standing: ^{1}H NMR (CD_3CN) major signals δ 0.95 (t, *J* = 7.0 Hz, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 8.21 (s, 1H); ^{11}B NMR (CD_3CN) δ -24.8 (d, *J* = 138 Hz, 4B), -17.4 (d, *J* = 150 Hz, 4B), 42.7 (s, 1B).

The crude acid extract was redissolved in 10% HCl (50 mL) and extracted with Et_2O (3 x 20 mL). The deep red organic layers were combined, and H_2O (10 mL) was added. The Et_2O was removed *in vacuo* giving a red film deposit. H_2O was decanted, and the red film was further washed with H_2O. The water was filtered, and any insoluble matter was recombined with the red film using CH_2Cl_2 (10 mL). $NMe_4^+Cl^-$ (0.093 g, 0.85 mmol) dissolved in H_2O (10 mL) was added, and the biphasic mixture was vigorously stirred for 1 hr. The deep red organic layer slowly began to turn light orange as a result. The organic layer was separated, and the H_2O was further extracted with CH_2Cl_2. The organic layers were combined, dried (Na_2SO_4), and solvent evaporated giving 320 mg (67% yield) of ~60% pure **5[NMe$_4$]** (contains ~40% NMP by ^{1}H NMR) as a yellow/orange viscous film: ^{1}H NMR (CD_3CN) major signals δ 0.93 (t, *J* = 7.0 Hz, 3H), 1.57 (quintet, *J* = 7.0 Hz, 2H), 3.05 (s, 12H), 6.96 (d, *J* = 8.8 Hz, 2H), 7.77 (d, *J* = 8.8 Hz, 2H); ^{11}B NMR (CD_3CN) δ -24.8 (d, *J* = 139 Hz, 4B), -17.4 (d, *J* = 150 Hz, 4B), 42.6 (s, 1B);

MS (FAB): *m/z* 320-327 (M-H, max at 324, 100%); FAB-HRMS(-): calcd. for $C_{13}H_{26}B_9N_2O$ *m/z*: 325.2883; found; 325.2877.

Preparation of *N*-Butyl-4-heptyloxypyridinium bromide (7)

4-Heptyloxypyridine[2] (1.00 g, 5.2 mmol) and 1-bromobutane (1.67 mL, 15.6 mmol) dissolved in anhydrous CH_3CN (10 mL) were stirred at reflux for 6 hrs. Solvent was removed *in vacuo*, and the crude product (1.68 g) was passed through a short silica gel plug (CH_3CN/CH_2Cl_2, 1:9) giving 1.30 g (77% yield) of the pure salt **7** as a colorless oil, which slowly crystallized: mp 34 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, *J* = 6.7 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H), 1.26-1.40 (m, 10H), 1.82 (quintet, *J* = 7.1 Hz, 2H), 1.95 (quintet, *J* = 7.2 Hz, 2H), 4.24 (t, *J* = 6.3 Hz, 2H), 4.70 (t, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 6.5 Hz, 2H), 9.21 (d, *J* = 6.6 Hz, 2H); UV (MeCN) λ_{max} 246 nm (log ε = 4.20), (CH_2ClCH_2Cl) λ_{max} 244 nm (log ε = 4.6). Anal. Calcd. for $C_{16}H_{28}BrNO$: C, 58.18; H, 8.54; N, 4.24; Found: C, 56.06; H, 8.77; N, 4.40.

Preparation of [*closo*-1-CB_9H_8-1-(N=N-C_6H_4-OH-4)-10-I]$^-NMe_4^+$ (9[NMe_4])

[*Closo*-1-CB_9H_8-1-N_2-10-I] (**11**, 0.368 g, 1.14 mmol) was slowly added to a solution of $NMe_4^+OH^- \cdot 5H_2O$ (2.5 g, 13.60 mmol) and phenol (1.27 g, 13.5 mmol) in H_2O/CH_3CN (1:4 vol/vol) at 5 °C. Upon addition of **11**, an orange solution formed. The reaction was warmed to rt, and stirring continued for 1 hr. The reaction mixture was acidified with 10 % HCl and CH_3CN was removed *in vacuo*. The aqueous solution was extracted with Et_2O (3 x 20 mL), or until the organic layer was no longer colored. The organic layers were combined, dried (Na_2SO_4), and solvent evaporated giving 1.65 g of a crude product as a red/orange oil. The

crude product was purified by column chromatography (SiO_2, CH_3CN/CH_2Cl_2, 1:6) giving 0.531 g of [*closo*-1-CB_9H_8-1-(N=N-C_6H_4-OH-4)-10-I]$^-H_3O^+$ (**9[H_3O]**) as a yellow/orange film that slowly crystallized: ^{1}H NMR (CD_3CN) δ 6.97 (d, *J* = 8.8 Hz, 2H); 7.80 (d, *J* = 8.8 Hz, 2H); ^{11}B {^{1}H} NMR (CD_3CN) δ -20.5 (4B), -16.1 (4B), 17.3 (1B).

The crude phenol was redissolved in Et_2O (10 mL), H_2O (8 mL) was added, and the Et_2O was removed *in vacuo*. The mother liquor was separated from a yellow insoluble material (0.105 g), and NMe_4^+ Cl^- (0.125 g, 1.14 mmol) was added to the mother liquor. The precipitate was filtered and dried *in vacuo* giving 0.356 g of **9[NMe_4]** as a yellow solid. ^{1}H and ^{11}B NMR analysis demonstrated that the insoluble material from removal of Et_2O was also **9[NMe_4]**. The combined yield of **9[NMe_4]** was 0.461 g (93% yield). A small portion of the product was recrystallized from hot CH_3OH/H_2O layered with hexane, which upon cooling gave yellow crystalline leaflets for analysis: mp 100 ^{o}C dec; ^{1}H NMR (CD_3CN) δ 0.4-2.50 (m, 8H, B-H), 3.05 (s, 12H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.45 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H); ^{11}B NMR (CD_3CN) δ -20.5 (d, *J* = 148 Hz, 4B), -16.1 (d, *J* = 160 Hz, 4B), 17.2 (s, 1B). Anal. Calcd. for $C_{11}H_{25}B_9IN_3O$: C, 30.06; H, 5.73; N, 9.56. Found: C, 29.47; H, 5.95; N, 9.21.

Characterization of [*closo*-1-CB_9H_8-1-COOH-10-PCy_3] (10).

Phosphonium zwitterion **10** was isolated from the main fraction of acid **3[H_3O]** separated by chromatography from the reaction mixture of iodo acid **8[NMe_4]** (0.225 g, 0.62 mmol), hexylzinc chloride (3.1 mmol), $[HPCy_3]^+BF_4^-$ (0.018 g, 0.050 mmol), and Pd_2dba_3 (0.011 g, 0.012 mmol) as described above. Thus, washing the acid fraction (0.192 g) with CH_3OH gave 10 mg (~ 3% yield) of insoluble material identified as the phosphonium zwitterion **10**: ^{1}H NMR (acetone-d_6) δ 0.40-2.50 (m, 8H, B-H), 1.30-1.48 (m, 10H), 1.74-1.76 (m, 3H),

1.81-1.91 (m, 11H), 2.22-2.25 (m, 6H), 2.66 (q, J = 11.9 Hz, 3H), COOH not observed; ^{11}B NMR (acetone-d_6) δ -19.5 (d, J = 125 Hz, 4B), -13.4 (d, J = 158 Hz, 4B), 21.7 (d, J = 189 Hz, 1B); MS (FAB): *m/z* 439-445 (M-H, max at 443, 100%); FAB-HRMS(+): calcd. for $C_{20}H_{42}B_9O_2P$ *m/z*: 444.3760; found; 444.3758.

Preparation of [*closo*-1-CB_9H_8-1-N_2-10-I] (11).[3]

A suspension of [*closo*-1-CB_9H_8-1-NHBoc-10-I]$^-$ NEt_4^+ (**12[NEt_4]**, 1.18 g, 2.41 mmol) in a 1:3 mixture of conc. HCl and CH_3OH (50 mL) was heated gently until all solids dissolved, and stirring was continued at rt for 18 hrs. H_2O (20 mL) was added and CH_3OH was removed *in vacuo*. Conc. HCl (3 mL) was added, and the resulting solution was extracted with Et_2O (3 x 30 mL). The organic layers were combined, dried (Na_2SO_4), and solvents evaporated *in vacuo* to give 0.604 g of crude [*closo*-1-CB_9H_8-1-NH_3-10-I] as a transparent film, which slowly solidified as a light brown glass:[1] ^{1}H NMR (CD_3CN) δ 8.55 (s); ^{11}B NMR (CD_3CN) δ -21.3 (d, J = 145 Hz, 4B), -16.3 (d, J = 156 Hz, 4B), 16.9 (s, 1B); IR 3185 and 3123 (N-H) cm^{-1}.

The crude product was dissolved in a 1:1 mixture of AcOH/H_2O (6 mL), and an aqueous solution of $NaNO_2$ (0.183 g, 2.65 mmol) in H_2O (4 mL) was added dropwise (~1 drop/sec) at 0 °C. Immediately, a white precipitate began to form. The reaction temperature was maintained for 30 min, H_2O (2 mL) was added, and the precipitate was filtered and dried to give 0.577 g (88% yield) of **11** as a white crystalline solid: mp 106 °C dec; ^{1}H NMR (CD_3CN) δ 1.28 (q, J = 156 Hz, 4H), 2.59 (q, J = 170 Hz, 4H); ^{11}B NMR (CD_3CN) δ -18.3 (d, J = 152 Hz, 4B), -8.8 (d, J = 169 Hz, 4B), 34.6 (s, 1B); IR 2245 (N_2) cm^{-1}.

Preparation of [*closo*-1-CB_9H_8-1-NHBoc-10-I]$^-$$NEt_4^+$ (12[NEt_4]).

A suspension of acid[1] [*closo*-1-CB_9H_8-1-COOH-10-I]$^-NEt_4^+$ (**8[NMe_4]**, 2.94 g, 7.02 mmol) in anhydrous CH_2Cl_2 (30 mL) was treated with neat $(COCl)_2$ (0.65 mL, 7.72 mmol). Vigorous bubbling of CO and CO_2 gases was observed followed by the dissolution of the substrate and the formation of a clear slight yellow solution. The solution was stirred for 1 hr at rt followed by filtration to remove insoluble particulates. The mother liquor was evaporated to dryness giving 3.10 g of crude [*closo*-1-CB_9H_9-1-COCl]$^-$ NEt_4^+ as a white solid: ^{11}B {^1H} NMR δ (CD_3CN) -19.3 (4B), -13.6 (4B), 23.4 (1B); IR 2582 (B-H), 1772 (C=O) cm^{-1}.

Crude [*closo*-1-CB_9H_8-1-COCl-10-I]$^-$ NEt_4^+ (3.10 g, 7.02 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL) and added via syringe to solid anhydrous $ZnCl_2$ (0.096 g, 0.702 mmol) under N_2 atmosphere. The reaction mixture was cooled to 0 °C, and Me_3SiN_3 (1.01 mL, 7.72 mmol) was added at once. The reaction mixture was stirred at 0 °C for an additional 30 min after which it was stirred for 4 hrs at rt. The reaction mixture was poured into ice-cold H_2O (50 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and solvent was removed *in vacuo* giving 3.09 g of crude [*closo*-1-CB_9H_8-1-CON_3-10-I]$^-$ NEt_4^+ as a white crystalline solid: ^{11}B {^1H} NMR (CD_3CN) δ -19.7 (4B), -14.9 (4B), 21.5 (1B); IR 2570 and 2523 (B-H), 2137 (N_3), 1686 (C=O) cm^{-1}. The crude product was contaminated with about 15% of [*closo*-1-CB_9H_8-1-COOH-10-I]$^-NEt_4^+$ (**8[NEt_4]**)

Crude [*closo*-1-CB_9H_8-1-CON_3-10-I]$^-$ NEt_4^+ (3.09 g, 6.96 mmol) was dissolved in anhydrous CH_3CN (30 mL) and refluxed for 1 hr. The reaction was cooled to rt, solvent removed, and the residue was dried *in vacuo* giving 2.90 g of crude [*closo*-1-CB_9H_8-1-NCO-10-I]$^-$ NEt_4^+ as a slight yellow solid: ^{11}B {^1H} NMR (CD_3CN) δ -22.0 (4B), -15.5 (4B), 13.8 (1B); IR 2564 and 2525 (B-H), 2265 (N=C=O) cm^{-1}.

A solution of anhydrous *tert*-butanol (3.33 mL, 34.85 mmol), anhydrous CH_3CN (30 mL), and crude [*closo*-1-CB_9H_8-1-NCO-10-I]$^-$ NEt_4^+ (2.90 g, 6.97 mmol) was stirred at reflux for 2 hr after which solvents were removed leaving 3.06 g of crude **12[NEt$_4$]** as a yellow solid. The crude solid was dissolved in CH_2Cl_2 and passed through a silica gel plug first washed with 2% NEt_3 in CH_2Cl_2. Elution with a buffered CH_3CN/CH_2Cl_2 solution (2% NEt_3, 10% CH_3CN, 88% CH_2Cl_2) afforded 1.98 g (53% yield based on starting acid [*closo*-1-CB_9H_8-1-COOH-10-I]$^-$ NEt_4^+) of pure **12[NEt$_4$]** as a slight yellow solid. A small portion of the product was recrystallized from aqueous EtOH for analysis: mp 156-158 ^oC; ^1H NMR (CD_3CN) δ 0.40-2.50 (m, 8H, B-H), 1.20 (t, *J* = 7.2 Hz, 12H), 1.48 (s, 9H), 3.15 (q, *J* = 7.2 Hz, 8H), 7.08 (s, 1H); ^{11}B NMR (CD_3CN) δ -22.1 (d, *J* = 142 Hz, 4B), -16.7 (d, *J* = 155 Hz, 4B), 13.0 (1B); IR 3305 and 3233 (N-H), 2564 and 2520 (B-H), 1679 (C=O) cm^{-1}. Anal. Calcd. for $C_{14}H_{38}B_9IN_2O_2$: C, 34.27; H, 7.81; N, 5.71. Found: C, 34.32; H, 7.79; N, 5.71.

Further elution gave 0.75 g of a 90:10 mixture of **12[NEt$_4$]** and staring acid [*closo*-1-CB_9H_8-1-COOH-10-I]$^-$ NEt_4^+ (**8[NEt$_4$]**).

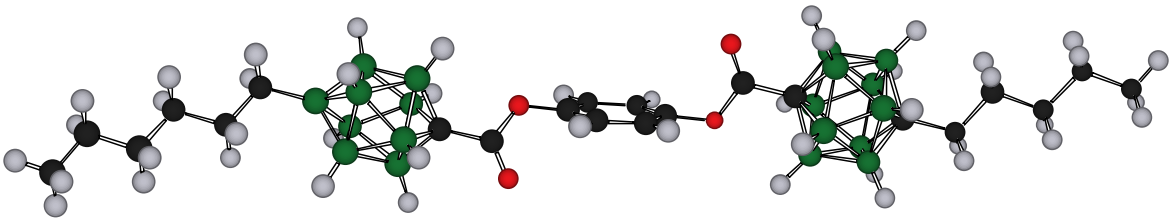
4. Computational Details

Geometry optimization for **1d[Pyr]**, **1f[Pyr]**, and **2d[Pyr]** was undertaken without symmetry constraints and default convergence limits with the HF/6-31G(d) method using the Gaussian 98 computational package.[4] The optimized geometries of the models were perturbed several times to assure conformational minimum and the fully optimized structures are shown in Figure S9.

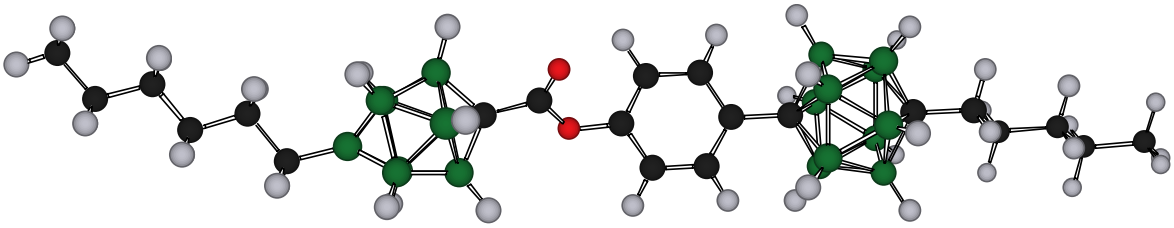
Geometry optimizations with smaller basis set (3-21G*) gave the unrealistic dihedral angle between the carboxyl group and the phenyl ring (COO–Ph). While the angle typically

found in solid-state structures is in the range of 45°–90°, the HF/3-21G(d) level calculations optimized these two groups as coplanar. Realistic geometries were obtained using the HF/6-31G(d) method.

1d



1f



2d

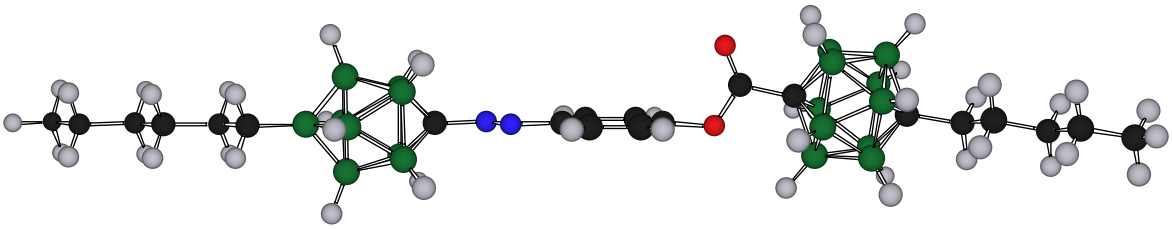


Figure S9. Molecular structures of anions **1d**, **1f**, and **2d** obtained by full geometry optimization at the HF/6-31G(d) level of theory.

5. Archive for HF/6-31G(d) computational results

1d[Pyr]

```
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1f[Pyr]

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2d[Pyr]

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2)]\\@

N-Butyl-4-heptyloxypyridine (7)

1\1\GINC-MONSTER\FOpt\RHF\6-31G(d)\C16H28N1O1(1+)\PIOTR\10-Apr-2009\0\
\#P HF/6-31G* FOPT GEOM(NOANGLE,NODISTANCE) FCHECK\\N-Butyl-4-heptylox
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,1.5710664884\C,0.1379665964,0.1708898476,2.9128926094\N,-0.996797342,
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4. Gaussian 98, Revision A.9, 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, 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.