Supplementary Material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information for

Polar Derivatives of the [*closo*-1-CB_9H_{10}]$^-$ Cluster as Positive $\Delta\varepsilon$ Additives to Nematic Hosts

Bryan Ringstrand, Piotr Kaszynski,* and Adam Januszko

Organic Materials Research Group

Department of Chemistry, Vanderbilt University, Nashville, TN 37235

Victor G. Young Jr.

X-ray Crystallographic Laboratory

Department of Chemistry
University of Minnesota, Twin Cities, MN 55455

Table of Content:

1. Synthetic and characterization details

Reagents and solvents were obtained commercially. Solvents were dried and deoxygenated before use, and reagents were used as supplied. $ZnCl_2$ was dried by heating at ~100 ^oC under vacuum. The concentration of Grignard or organozinc reagents were determined by I_2 titration.[1] Reactions were carried out under dry Ar, subsequent manipulations conducted in air.

NMR spectra were obtained at 128.4 MHz (^{11}B) and 400.1 MHz (^1H) in CD_3CN or $CDCl_3$ unless otherwise specified. ^1H NMR spectra were referenced to CD_3CN (1.93 ppm) or $CDCl_3$ (7.24 ppm). ^{11}B NMR chemical shifts are relative to the resonance of an external boric acid sample in CH_3OH that was set to 18.1 ppm. IR spectra were recorded in the solid state using an AT-IR accessory. Elemental analysis was provided by Atlantic Microlab, GA.

Thermal analysis was obtained using a TA Instruments 2920 differential scanning calorimeter (DSC). Transition temperatures (onset) and enthalpies were obtained using small samples (0.3-0.6 mg) and a heating rate of 5 K min^{-1} under a flow of nitrogen gas.

UV spectra were recorded in UV-grade CH_3CN. All compounds were in concentration of 0.4–4 x 10^{-5} M. Extinction coefficients were obtained by fitting the maximum absorbance against concentration in agreement with Beer's law.

Preparation of [*closo*-1-CB_9H_8-1-$NC_{12}H_{23}$-10-C_6H_{13}] (1)

A mixture of [*closo*-1-CB_9H_8-1-NH_2-10-C_6H_{13}]$^-$ NMe_4^+ (**4[NMe_4]**, 0.190 g, 0.65 mmol), 3,3-bis(2-bromoethyl)-1-bromooctane[2] (**9**, 0.26 g, 0.65 mmol), 18-crown-6 (0.011 g, 0.042 mmol), and anhydrous K_2CO_3 (0.248 g, 1.79 mmol) were refluxed in anhydrous CH_3CN (20 mL) under inert atmosphere for 9 days. The reaction mixture was filtered, washed with CH_2Cl_2,

and solvents removed giving a semi-crystalline yellow-brown solid. The solid was passed through a short silica-gel plug (CH_2Cl_2) giving 0.270 g of crude product, which was washed with iso-octane and cold CH_3OH giving 0.130 g of a white residue. The white residue was further purified via column chromatography (hexanes/CH_2Cl_2, 1:2) giving 0.080 g (33% yield) of [*closo*-1-CB_9H_8-1-$NC_{12}H_{23}$-10-C_6H_{13}] (**1**) as a white crystalline solid. The final product was further purified by recrystallization (iso-octane/toluene mixture): mp 363 °C dec (DSC); ^{1}H NMR ($CDCl_3$) δ 0.40-2.80 (br m, 8H), 0.80-1.00 (m, 6H), 1.12-1.50 (m, 10H), 1.52-1.70 (m, 4H), 1.81-1.95 (m, 2H) 2.01-2.15 (m, 8H), 4.10-4.30 (m, 6H); ^{11}B NMR ($CDCl_3$) δ -26.4 (d, *J* = 141 Hz, 4B), -18.5 (d, *J* = 110 Hz, 4B), 46.4 (s, 1B). Anal. Calcd. for $C_{19}H_{44}B_9N$: C, 59.45; H, 11.55; N, 3.65. Found: C, 59.57; H, 11.65; N, 3.78.

Preparation of [*closo*-1-CB_9H_8-1-$SC_{10}H_{20}$-10-C_6H_{13}] (2)

To a three-necked flask under inert atmosphere attached with reflux condenser, a glass stopcock, and septum containing Pd_2dba_3 (5 mg, 0.005 mmol) and [$HPCy_3$]BF_4 (8 mg, 0.022 mmol) was added an anhydrous NMP/THF mixture (6 mL, 1:2). A solution $C_6H_{13}ZnCl$ (3 mL, 2.14 mmol, 0.712 M) [prepared from $C_6H_{13}MgBr$ (3 mL, 2.14 mmol, 0.712 M) and anhydrous $ZnCl_2$ (0.300 g, 2.20 mmol)] was added resulting in the formation of a yellow/orange suspension that slowly turned green. [*closo*-1-CB_9H_8-1-$SC_{10}H_{20}$-10-I] (**10**, 0.114 g, 0.274 mmol) dissolved in anhydrous THF (2 mL) was added via syringe, the septum replaced with a glass stopcock, and the reaction was stirred at 85 °C. Reaction progress was monitored at 24 hr intervals by ^{11}B NMR analysis. If the reaction was incomplete, additional equivalents of Pd_2dba_3, [$HPCy_3$]BF_4, and $C_6H_{13}ZnCl$ were added and stirring continued at 85 °C. After 72 hr, the reaction was quenched with a saturated solution of NH_4Cl (10 mL), extracted into Et_2O (3 x

5 mL), dried (Na_2SO_4) and evaporated. NMP was removed via vacuum distillation (0.5 mm Hg, 50 °C) giving 0.212 g of crude product. The crude product was purified via column chromatography (CH_2Cl_2/hexane, 1:1) giving 0.060 g (58% yield) of [*closo*-1-CB_9H_8-1-$SC_{10}H_{20}$-10-C_6H_{13}] (**2**) as a yellowish solid. The final product was further purified by washing with hot hexane and recrystallization (toluene/iso-octane mixture): mp 209 °C (DSC); ^{1}H NMR ($CDCl_3$) δ 0.40-2.80 (br m, 8H), 0.92 (t, *J* = 6.5 Hz, 6H), 1.33-1.40 (m, 13H), 1.51-1.63 (m, 2H), 1.62-1.80 (m, 2H), 1.85-1.95 (m, 2H), 2.05-2.14 (m, 2H), 2.50 (br d, *J* = 11.6 Hz, 2H), 3.60-3.72 (m, 2H), 4.07 (br d, *J* = 11.7 Hz, 2H); ^{11}B NMR ($CDCl_3$) δ -24.5 (d, *J* = 146 Hz, 4B), -16.2 (d, *J* = 149 Hz, 4B), 54.1 (s, 1B). Anal. Calcd. for $C_{17}H_{41}B_9S$: C, 54.47; H, 11.02. Found: C, 54.69; H, 11.17.

Preparation of [*closo*-1-CB_9H_8-1-NH_2-10-C_6H_{13}]$^-$ NMe_4^+ (4[NMe_4])

To a three-necked flask under inert atmosphere attached with reflux condenser, a glass stopcock, and septum containing iodo amine[3] [*closo*-1-CB_9H_8-1-NH_2-10-I]$^-$ $NHMe_3^+$ (**3[$NHMe_3$]**, 0.635 g, 1.98 mmol) [^{11}B NMR (CD_3CN) δ -22.0 (d, *J* = 144 Hz, 4B), -16.3 (d, *J* = 157 Hz, 4B), 10.8 (1B)] dissolved in anhydrous THF (20 mL) was added $C_6H_{13}MgBr$ (9.9 mL, 19.8 mmol, 2.0 M). A bubbler was attached, and the reaction mixture was heated at reflux for 30 min. $(PPh_3)_2PdCl_2$ (0.186 g, 0.26 mmol) and CuI (0.075 g, 0.393 mmol) were added, and the reaction was stirred at reflux, and reaction progress was monitored by ^{11}B NMR at 24 hr intervals. If the reaction was incomplete, additional equivalents of $C_6H_{13}MgBr$, $(PPh_3)_2PdCl_2$, and CuI were added and heating continued. A 5% HCl solution (200 mL) was added, and the reaction mixture was extracted with Et_2O (3 x 50 mL). The organic layers were combined, dried (Na_2SO_4), filtered, and evaporated giving 1.60 g of an oily brown residue. The residue

was purified by column chromatography (CH_3CN/CH_2Cl_2, 1:4) giving 0.140 g of crude acid extract [*closo*-1-CB_9H_8-1-NH_2-10-C_6H_{13}]$^-$ H_3O^+ [^{11}B {^{1}H} NMR (CD_3CN) δ -26.5 (4B), -18.1 (4B), 39.4 (1B)]. Water (5 mL) and NMe_4^+ OH^- · $5H_2O$ (0.109 g, 0.60 mmol) were added producing a milky suspension. Solvents were removed to dryness *in vacuo* giving 0.190 g (33% yield) of [*closo*-1-CB_9H_8-1-NH_2-10-C_6H_{13}]$^-$ NMe_4^+ (**4[NMe_4]**) as a colorless film that slowly crystallized: ^{1}H NMR (CD_3CN) δ 0.40-2.80 (br m, 8H), 0.91 (t, *J* = 7.0 Hz, 3H), 1.30-1.40 (m, 4H), 1.45-1.59 (m, 2H), 1.73-1.83 (m, 4H), 3.08 (s, 12H); ^{11}B {^{1}H} NMR δ -26.5 (4B), -18.2 (4B), 36.2 (1B); MS (FAB): *m/z* (216-220) max at 219 (100 %); FAB-HRMS(-): Calcd. for $C_8H_{22}B_9O_2$ *m/z*: 220.2668; found; 220.2670.

Identification of [*closo*-1-CB_9H_8-1-NH_2-10-PPh_3] (5).

Crude phosphonium adduct **5** (158 mg, 20% yield) of was isolated by column chromatography (CH_3CN/CH_2Cl_2, 1:9) during the purification of amine **4** as a slight yellow residue. An analytical sample was prepared by washing crude **5** with hot hexane, hot ethanol, and then recrystallized (cold toluene/CH_3CN mixture): mp 300 °C (DSC); ^{1}H NMR (CD_3CN) δ 7.57-7.65 (m, 6H), 7.69-7.76 (m, 3H), 7.78-7.88 (m, 6H); ^{11}B NMR (CD_3CN) δ -20.6 (d, *J* = 144 Hz, 4B), -14.5 (d, *J* = 154 Hz, 4B), 15.6 (d, *J* = 196 Hz, 1B); ^{31}P NMR (CD_3CN) δ 9.7 (q, *J* = 196 Hz); MS (FAB): *m/z* 393-398 (max at 396, 100%); FAB-HRMS(+): Calcd. for $C_{19}H_{25}B_9NP$ *m/z*: 397.2562; found; 397.2542. Anal. Calcd. for $C_{19}H_{25}B_9NP$: C, 57.67; H, 6.37; N, 3.54. Found: C, 56.87; H, 6.19; N, 3.33.

Preparation of [*closo*-1-CB_9H_8-1-$SCHN(Me)_2$-10-I] (8)

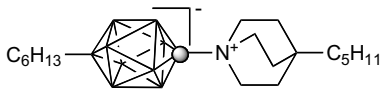
A yellow solution of [*closo*-1-CB_9H_8-1-N_2-10-I][3] (**7**, 0.200 g, 0.74 mmol) and freshly distilled Me_2NCHS (3.0 mL) was stirred at rt for 6 hr. Excess Me_2NCHS was removed by vacuum distillation (80 °C, 0.25 mm Hg) leaving 0.296 g of crude product as a slight yellow oil that slowly crystallized. The crude product was washed with toluene until the decant was no longer yellow giving 0.245 g (100% yield) of crude [*closo*-1-CB_9H_9-1-SCHN$(Me)_2$-10-I] (**8**) as yellowish solid: ^{1}H NMR (CD_3CN) (major signals) δ 3.46 (s, 3H), 3.65 (s, 3H), 9.74 (s, 1H), (minor signals attributed to Me_2NCHS) δ 3.19 (s, 3H), 3.25 (s, 3H), 9.14 (s, 1H); ^{11}B NMR (CD_3CN) δ -19.6 (d, J = 146 Hz, 4B), -13.9 (d, J = 156 Hz, 4B), 20.0 (s, 1B); MS (FAB): *m/z* (331-335) max at 333 (100 %); FAB-HRMS(+): Calcd. for $C_4H_{14}B_9INS$ *m/z*: 334.0729; found; 334.0731.

Preparation of [*closo*-1-CB_9H_8-1-$SC_{10}H_{20}$-10-I] (10)

A yellow solution of crude [*closo*-1-CB_9H_8-1-SCHN$(Me)_2$-10-I] (**8**, 0.245 g, 0.74 mmol), NMe_4^+ $OH^- \cdot 5H_2O$ (0.145 g, 0.80 mmol), and 1-bromo-3-(2-bromoethyl)octane[4] (0.220 g, 0.74 mmol) in anhydrous CH_3CN (5 mL) was stirred at rt for 12 hr. The reaction mixture was filtered and evaporated to dryness. The resulting residue was washed with hexane giving 0.43 g of crude product. The crude product was passed through a short silica gel plug (CH_2Cl_2/hexane, 1:1) giving 0.120 g (39% yield based on **7**) of [*closo*-1-CB_9H_8-1-$SC_{10}H_{20}$-10-I] (**10**) as the fast-moving component, which was further purified by recrystallization (toluene/iso-octane mixture): mp 230 °C; ^{1}H NMR (CD_3CN) δ 0.40-2.80 (br m, 8H), 0.90 (t, J = 6.9 Hz, 3H), 1.31-1.35 (m, 8H), 1.71-1.76 (m, 3H), 2.41 (m, 2H), 3.66 (t, J = 11.8 Hz, 2H), 4.13 (d, J = 11.1 Hz, 2H); ^{11}B NMR (CD_3CN) δ -19.8 (d, J = 152 Hz, 4B), -15.0 (d, J = 164 Hz, 4B), 23.2 (s, 1B). Anal. Calcd. for $C_{11}H_{28}B_9IS$: C, 31.71; H, 6.77. Found: C, 31.69; H, 6.86.

2. Thermal analysis of binary mixtures

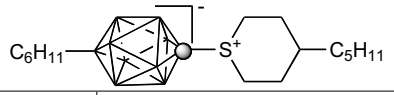
Table S1. T_{NI} for solutions of **1** in **ClEster**.



1

	mole fraction, *x*						
T_{NI}	0.00(host)	0.0152	0.0270	0.0332	0.0421	0.0491	0.0603
onset	47.3	48.8	49.7	50.2	51.25	51.8	52.6
peak	47.8	49.1	50.1	50.7	51.8	52.4	53.2

Table S2. T_{NI} for solutions of **2** in **ClEster**.



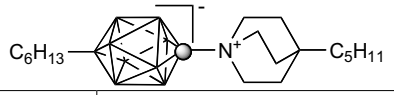
2

	mole fraction, *x*					
T_{NI}	0.00(host)	0.0246	0.0359	0.0538	0.0857	0.0949
onset	47.3	na	47.0	47.4	48.9	50.7
peak	47.8	na	47.7	48.4	50.5	51.9

3. Dielectric data for binary mixtures

Dielectric parameters in Tables S3 and S4 for low concentration solutions of additives **1** and **2** in **ClEster** were obtained by averaging 5-10 measurements of each solution in 2 cells. Standard deviation of the resulting values typically is ≤ ±0.02. All measurements were run at 25 °C. Error on concentration values ~1.5%.

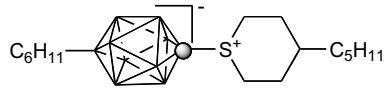
Table S3. Dielectric parameters for solutions of **1** in **ClEster** at 25 °C.



1

parameter	**mole fraction, *x***						
	0.00(host)	0.0152	0.0270	0.0332	0.0421	0.0491	0.0603
$\varepsilon_{\parallel}$	2.63±0.01	3.625±0.06	4.07±0.005	4.25±0.01	4.41±0.0	4.55±0.02	4.78±0.01
$\varepsilon_{\perp}$	3.22±0.01	3.38±0.01	3.45±0.00	3.49±0.004	3.49±0.015	3.52±0.01	3.57±0.01
$\Delta\varepsilon$	-0.59±0.01	0.24±0.06	0.63±0.006	0.76±0.01	0.93±0.02	1.03±0.01	1.21±0.01

Table S4. Dielectric parameters for solutions of **2** in **ClEster** at 25 °C.



2

parameter	mole fraction, *x*					
	0.00(host)	0.0246	0.0359	0.0538	0.0857	0.0949
$\varepsilon_{\|\|}$	2.63±0.01	4.13±0.05	4.54±0.04	4.99±0.01	5.68±0.04	5.87±0.04
$\varepsilon_{\perp}$	3.22±0.01	3.60±0.01	3.67±0.03	3.81±0.01	4.01±0.02	4.00±0.02
$\Delta\varepsilon$	-0.59±0.01	0.53±0.05	0.87±0.04	1.17±0.01	1.67±0.02	1.87±0.02

Using equations 1-3, dielectric parameters for each solution were extrapolated to the pure additive:

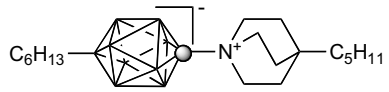
$$\Delta\varepsilon = x\Delta\varepsilon_a + (1-x)\Delta\varepsilon_{host} \qquad \text{equation 1}$$

$$\varepsilon_{\|} = x\varepsilon_{\|a} + (1-x)\varepsilon_{\|host} \qquad \text{equation 2}$$

$$\varepsilon_{\perp} = x\varepsilon_{\perp a} + (1-x)\varepsilon_{\perp host} \qquad \text{equation 3}$$

in which the subscript *a* denotes the additive and *x* its mole fraction. The resulting datapoints were fitted to a second order polynomial (see Figure 8 in the text).

Table S5. Extrapolated dielectric parameters for **1** at 25 °C.



1

extrapolated parameter	mole fraction, *x*					
	0.0152	0.0270	0.0332	0.0421	0.0491	0.0603
$\varepsilon_{\|\|}$	68.1±4.0	56.0±0.1	51.4±0.3	44.9±0.1	41.7±0.4	38.3±0.2
$\varepsilon_{\perp}$	13.9±0.6	11.7±0.1	11.4±0.1	9.6±0.4	9.3±0.2	9.0±0.2
$\Delta\varepsilon$	54.2±4.0	44.6±0.2	40.1±0.3	35.5±0.5	32.4±0.2	29.3±0.2

Best fit functions:

$\varepsilon_{\|} = 10552x^2 - 1458x + 88\pm1$; $r^2 = 0.999$

$\varepsilon_{\perp} = 2082x^2 - 269x + 17.5\pm1$; $r^2 = 0.980$

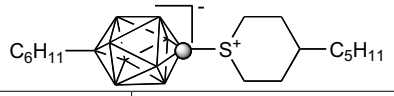
$\Delta\varepsilon = 8134x^2 - 1166x + 70\pm0.5$; $r^2 = 0.999$

$\varepsilon_{\|} = 3.74\pm0.1/(x - 0.0399\pm0.002)$; $r^2 = 0.997$

$\varepsilon_{\perp} = 1.02\pm0.1/(x - 0.0586\pm0.008)$; $r^2 = 0.965$

$\Delta\varepsilon = 2.80\pm0.05/(x - 0.0363\pm0.001)$; $r^2 = 0.999$

Table S6. Extrapolated dielectric parameters for **2** at 25 °C.



2

extrapolated parameter	**mole fraction, *x***				
	0.0246	0.0359	0.0538	0.0857	0.0949
$\varepsilon_{\|\|}$	63.6±2.0	55.8±1.1	46.5±0.2	38.2±0.5	36.8±0.4
$\varepsilon_{\perp}$	18.7±0.4	15.8±0.8	14.2±0.2	12.4±0.2	11.4±0.2
$\Delta\varepsilon$	44.9±2.0	40.1±1.1	32.1±0.2	25.8±0.3	25.3±0.2

Best fit functions:

$\varepsilon_{\|} = 4914x^2 - 962x + 84 \pm 1$; $r^2 = 0.999$

$\varepsilon_{\perp} = 1260x^2 - 244x + 23.5 \pm 2$; $r^2 = 0.973$

$\Delta\varepsilon = 3737x^2 - 730x + 61 \pm 1.5$; $r^2 = 0.998$

$\varepsilon_{\|} = 5.86 \pm 0.3/(x - 0.0685 \pm 0.006)$; $r^2 = 0.993$

$\varepsilon_{\perp} = 2.15 \pm 0.25/(x - 0.0941 \pm 0.016)$; $r^2 = 0.964$

$\Delta\varepsilon = 3.77 \pm 0.23/(x - 0.0595 \pm 0.006)$; $r^2 = 0.992$

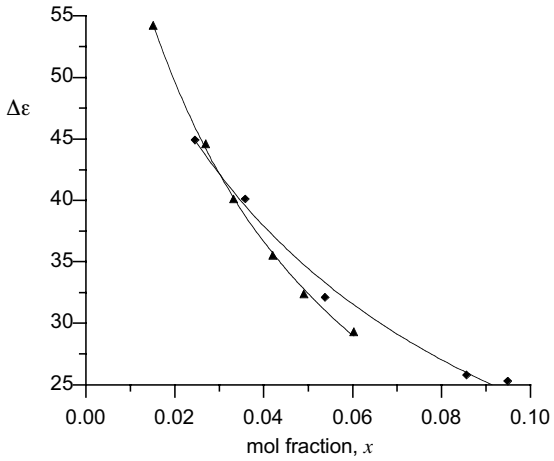


Figure S1. Extrapolated Δε *vs* concentration of **1** (triangles) and **2** (diamonds) in **ClEster** fitted to a hyperbolic function.

4. Details for calculations in the nematic phase

The Equations derived from the Maier-Meier theory used in this work were adopted from literature[5,6] and had the following form:

$$\Delta\varepsilon = \frac{NFh}{\varepsilon_0}\left\{\Delta\alpha - \frac{F\mu_{eff}^{\ 2}}{2k_BT}\left(1 - 3\cos^2\beta\right)\right\}S \qquad \text{equation 4}$$

$$\varepsilon_{\parallel} = 1 + \frac{NFh}{\varepsilon_0}\left\{\bar{\alpha} + \frac{2}{3}\Delta\alpha S + \frac{F\mu_{eff}^{\ 2}}{3k_B T}\left[1 - \left(1 - 3\cos^2\beta\right)S\right]\right\} \qquad \text{equation 5}$$

$$\varepsilon_{\perp} = 1 + \frac{NFh}{\varepsilon_0}\left\{\bar{\alpha} - \frac{1}{3}\Delta\alpha S + \frac{F\mu_{eff}^{\ 2}}{3k_B T}\left[1 + \frac{1}{2}\left(1 - 3\cos^2\beta\right)S\right]\right\} \qquad \text{equation 6}$$

All quantities were in SI units.

• Dielectric permittivity of vacuum:
$\varepsilon_0 = 1.114\times10^{-10}/4\pi = 8.865\times10^{-12}$ 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 $1.482 \times 4\pi\varepsilon_0 \times10^{-31} = 1.651\times10^{-41}$.

• 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 **1** and **2** assuming density of the liquid to be 1000 kg•m^{-3}, and expressed in molecules per m^3.

• For calculations involving the extrapolated dielectric parameters for each compound, reaction field factors *F* and *h* were calculated for the pure host **ClEster** using literature[5] values for mean α = 53.8×10^{-24} cm^{-3} (or 5.99×10^{-39} Cm^{2}V^{-1}) and experimental average permittivity ε = 3.03 taken as ε_s. The density was taken as 1.02 g cm^{-3}.[5] Thus, reaction field parameters *F* = 1.2090 and *h* = 1.2875 were obtained for **ClEster** using 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 assumed to be average dielectric permittivity calculated from $\varepsilon_{||}$ and $\varepsilon_{\perp}$.

5. Results of Maier-Meier analysis.

The order parameter *S* and the Kirkwood factor *g* for the zwitterionic additives were obtained by solving simultaneously equations for Δε and $\varepsilon_{||}$ (equations 4 and 5). The unknown *g* from the expression for Δε (equation 4) was substituted into the expression for $\varepsilon_{||}$ (equation 5) and solved for *S* (equation 7). In this form, order parameter *S* does not depend on the dipole moment μ, but depends on the dielectric permittivity components $\varepsilon_{||}$ and $\varepsilon_{\perp}$. The obtained value *S* was substituted to the expression for parameter *g* (equation 8).

$$S = \frac{\Delta\varepsilon\varepsilon_0}{\Delta\alpha NFh + (1-3\cos^2\beta)\left[\Delta\varepsilon\varepsilon_0 - \frac{3}{2}\left(\varepsilon_{\|}\varepsilon_0 - \varepsilon_0 - \overline{\alpha}NFh\right)\right]} \qquad \text{equation 7}$$

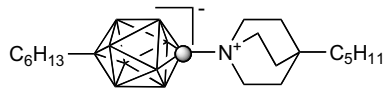
$$g = \frac{2(\Delta\alpha NFhS - \Delta\varepsilon\varepsilon_0)k_BT}{NF^2h\mu^2(1-3\cos^2\beta)S} \qquad \text{equation 8}$$

The protocol was verified by substituting the computed parameters S and g into equations 4-6 and calculating back the dielectric parameters.

Molarity of solutions of **1** and **2** was calculated using the literature[5] value for the density of the host (1.02 g cm^{-3}) and it was used to derive the equilibrium constant *K* using equation 9:

$$g = \frac{\sqrt{8Kc+1}-1}{4Kc} \qquad \text{equation 9}$$

Table S7. Calculated apparent order parameter S_{app} and Kirkwood constant g for solutions of **1** in **ClEster** at 25 °C.



1

parameter	**mole fraction, *x***					
	0.0152	0.0270	0.0332	0.0421	0.0491	0.0603
	concentration, *c* /molL^{-1}					
	0.0337	0.0600	0.0739	0.0937	0.1096	0.1348
	Using dipole moment μ calculated for ε = 1					
S_{app}	0.64	0.645	0.62	0.64	0.63	0.62
g	0.380	0.310	0.287	0.244	0.228	0.211
	Using dipole moment μ calculated for ε = 3.03 (host medium)					
S_{app}	0.64	0.64	0.63	0.65	0.64	0.62
g	0.301	0.245	0.227	0.193	0.180	0.167
	Using dipole moment μ calculated for ε of each solution					
S_{app}	0.64	0.65	0.63	0.65	0.64	0.63
g	0.294	0.235	0.216	0.183	0.170	0.155
	Using dipole moment μ and field parameters F and h calculated for ε of each solution					
S_{app}	0.65	0.65	0.63	0.65	0.64	0.63
g	0.279	0.218	0.199	0.167	0.154	0.140

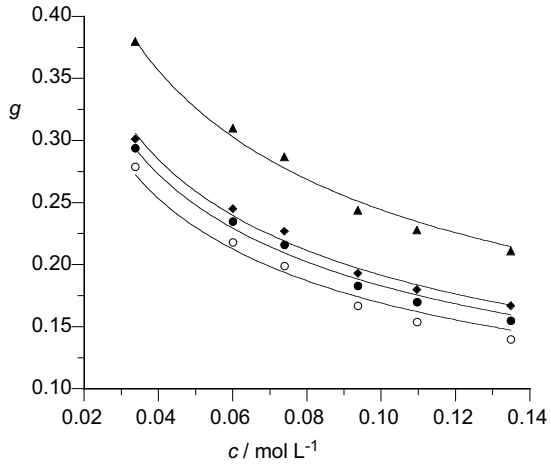
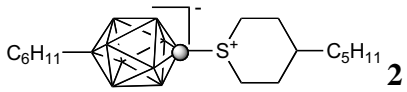


Figure S2. A plot of g values (Table S7) calculated for different concentration of **1** in **ClEster** using model 1 (triangles), model 2 (diamonds), model 3 (filled circles), and model 4 (open circles). Equation 9 is the fitting function.

Table S8. Calculated apparent order parameter S_{app} and Kirkwood constant g for solutions of **2** in **ClEster** at 25 °C.



2

parameter	**mole fraction, *x***				
	0.0246	0.0359	0.0538	0.0857	0.0949
	concentration, *c* /molL^{-1}				
	0.0521	0.0746	0.1084	0.1641	0.1791
	Using dipole moment μ calculated for ε = 1				
S_{app}	0.50	0.52	0.49	0.48	0.50
g	0.423	0.362	0.305	0.252	0.236
	Using dipole moment μ calculated for ε = 3.03 (host medium)				
S_{app}	0.50	0.52	0.50	0.48	0.51
g	0.339	0.290	0.244	0.201	0.189
	Using dipole moment μ calculated for ε of each solution				
S_{app}	0.51	0.53	0.50	0.49	0.51
g	0.324	0.273	0.226	0.181	0.169
	Using dipole moment μ and field parameters F and h calculated for ε of each solution				
S_{app}	0.51	0.53	0.51	0.49	0.52
G	0.297	0.246	0.200	0.155	0.144

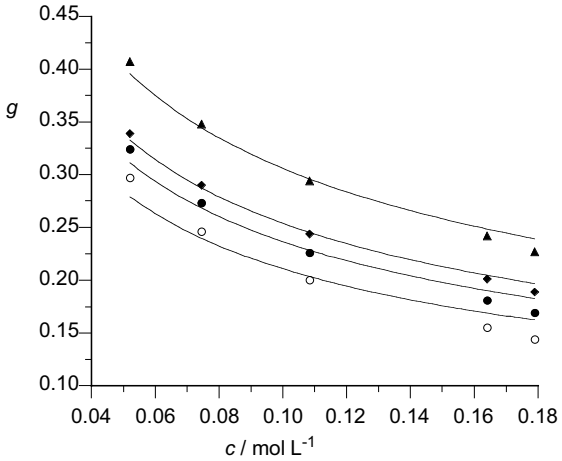


Figure S3. A plot of g values (Table S8) calculated for different concentration of **2** in **ClEster** using model 1 (triangles), model 2 (diamonds), model 3 (filled circles), and model 4 (open circles). Equation 9 is the fitting function.

6. Dipole moment and polarizability computational results for 1 and 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)

Quinuclidinium 1

```
gas phase, ε = 1.0:    X= 15.8566 Y= 2.8579 Z= 0.0110  Tot= 16.1121
IPCM,      ε = 2.84:   X= 17.6353 Y= 3.5504 Z= 0.2557  Tot= 17.9910
IPCM,      ε = 3.03:   X= 17.7648 Y= 3.6423 Z= 0.2757  Tot= 18.1364
IPCM,      ε = 4.00:   X= 18.1664 Y= 3.7948 Z= 0.3527  Tot= 18.5618
```

Linear dependence on dielectric permittivity for **1**
$\mu_x(\varepsilon) = 0.802\varepsilon + 15.18$ ($r^2 = 0.962$)
$\mu_y(\varepsilon) = 0.325\varepsilon + 2.58$ ($r^2 = 0.966$)
$\mu_z(\varepsilon) = 0.125\varepsilon - 0.12$ ($r^2 = 0.977$)

Sulfonium 2

```
gas phase, ε = 1.0:    X= 15.2675 Y= 1.1938 Z= 2.3588  Tot= 15.4947
IPCM,      ε = 2.84:   X= 16.8698 Y= 1.5756 Z= 2.9909  Tot= 17.2052
IPCM,      ε = 3.03:   X= 16.9800 Y= 1.6108 Z= 3.0326  Tot= 17.3238
IPCM,      ε = 4.62:   X= 17.7271 Y= 1.9005 Z= 3.3396  Tot=  18.1388
```

Linear dependence on dielectric permittivity for **2**
$\mu_x(\varepsilon) = 0.686\varepsilon + 14.74$ ($r^2 = 0.964$)
$\mu_y(\varepsilon) = 0.196\varepsilon + 1.01$ ($r^2 = 0.998$)
$\mu_z(\varepsilon) = 0.273\varepsilon + 2.15$ ($r^2 = 0.968$)

Electronic polarizabilities (au) at the B3LYP/3-21G level of theory (full geometry optimization) $1 Å^3 = 0.1482$ au

Quinuclidinium 1

```
Exact polarizability: 411.848 5.503 246.545 -0.329 -0.162 239.097
Diagonalized: 412.0, 246.4, 239.1
```

Sulfonium 2

```
Exact polarizability: 418.344 2.546 242.140 7.870 4.595 246.833
Diagonalized: 418.7, 249.3 239.3
```

7. X-ray crystallography procedures

A colorless crystal (approximate dimensions 0.020 x 0.010 x 0.005 mm^3) was placed onto the tip of ultra thin glass fiber and mounted on a SMART Platform 3-circle diffractometr equipped with a SMART6000 (Bruker) detector and measured at 95(2) K.

Data collection

The data collection was carried out using synchrotron radiation (λ = 0.49595, double-diamond 111 monochromators, two mirrors to exclude higher harmonics) with a frame time of 1 second and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to the extent of 2.0 hemispheres. Two major sections of frames were collected with 0.30° steps in ω and ϕ with a detector position of 0° in 2θ. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from 2742 strong reflections from the actual data collection after integration (SAINT).[7] The intensity data were corrected for absorption (SADABS).[8]

Structure solution and refinement

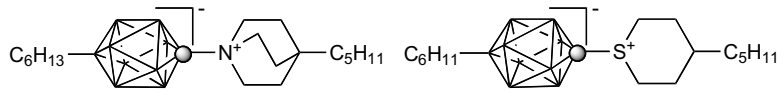
The space group P-1 was determined based on intensity statistics and systematic absences. The structure was solved using SHELXS-97[9] and refined with SHELXL-97.[10] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with individual relative isotropic displacement parameters. The final full matrix least squares refinement converged to R1 = 0.0641 and wR2 = 0.1859 (F^2, all data). The remaining electron density is located.

Table S9. Crystallographic Data for **1**.

chemical formula	$C_{19}H_{44}B_9N$
formula weight	383.84
crystal color, shape, size	colorless plate, 0.020 x 0.010 x 0.005 mm^3
temperature,	95(2) K
wavelength, λ	0.49595 Å
system, space group	triclinic, P-1
Unit cell dimensions	
a	9.766(2) Å
b	10.481(3) Å
c	12.098(3) Å
α	93.804(9)°
β	90.249(10)°
γ	102.587(10)°
volume	1205.7(5) $Å^3$
Z	2
Density (D_{calcd})	1.057 Mg/m^3
Absorption coefficient μ	0.013 mm^{-1}
F(000)	420
Theta range for data collection	2.91 to 17.46°.
Index ranges	$-11 \le h \le 11, -12 \le k \le 12, 0 \le l \le 14$
Reflections collected	18929
Independent reflections	4348 [R(int) = 0.0645]
Observed Reflections	3664
Completeness to theta = 17.46°	97.0 %
Solution and Refinement	
Absorption correction	Multi-scan
Max. and min. transmission	0.99 and 0.98
Solution	Direct methods
Refinement method	Full-matrix least-squares on F^2
Weighting scheme	$w = [\sigma^2 Fo^2 + AP^2 + BP]^{-1}$, with $P = (Fo^2 + 2\,Fc^2)/3$, A = , B =
Data / restraints / parameters	4348 / 0 / 264
Goodness-of-fit on F^2	1.079
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1789
R indices (all data)	R1 = 0.0747, wR2 = 0.1859
Largest diff. peak and hole	0.360 and -0.298 $e.Å^{-3}$

8. Structural Data

Table S10. Selected Experimental and Calculated Selected Bond Lengths and Angles for **1** and **2**.



1 **2**

	1 (C_1)		**2** (C_1)
Distances /Å	Experimental	HF/6-31G(d)	HF/6-31G(d)
C_{cage}–X	1.505(2)	1.498	1.761
B(10)–C_{alk}	1.593(3)	1.601	1.601
B–C_{cage} (avrg)	1.619(3)	1.615	1.611
B–B(10) (avrg)	1.715	1.713	1.715
C–X (avrg)	1.525	1.508	1.816
B···C [a]	7.70	7.57	7.99
Angles / [o]			
B-C(1)-B (avrg)	70.0	70.2	70.9
C_β–C_α–B(10)–B	56.1(2)	51.7	48.5
C–X–C_{cage}–B	8.6(2)	0.1	52.1
C_β–C_α–C_{ring}–C_{ring}	172.1(2)	173.4	171.1
chain–chain[b]	11	23	41

[a] Length of the molecular rigid core. [b] Interplanar angle defined by the first three carbon atoms in each aliphatic chain.

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

1

```
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```

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2

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