Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Data to

Polyfluorinated carba-*closo*-dodecaboranes with amino and ammonio substituents bonded to boron

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Table S1 Crystal data and structure refinement parameters for 1-H-12-H_3N-*closo*-1-$CB_{11}F_{10}$·H_2O (H**1**·H_2O), 1-H-7-H_3N-*closo*-1-$CB_{11}F_{10}$·diglyme (H**2**·diglyme), 1-H-2-H_3N-*closo*-1-$CB_{11}F_{10}$·0.5H_2O (H**3**·0.5H_2O), [Et_4N][1-H-12-H_2N-*closo*-1-$CB_{11}F_{10}$] ([Et_4N]**1**) and 7-H_3N-12-F-*closo*-1-$CB_{11}H_{10}$·$(CH_3)_2CO$ (H**4**·$(CH_3)_2CO$).

Compound	H**1**·H_2O	H**2**·diglyme	H**3**·0.5H_2O	[Et_4N]**1**	H**4**·$(CH_3)_2CO$
Formula	$CH_6B_{11}F_{10}NO$	$C_7H_{18}B_{11}F_{10}NO_3$	$CH_5B_{11}F_{10}NO_{0.5}$	$C_9H_{23}B_{11}F_{10}N_2$	$C_4H_{19}B_{11}FNO$
Formula weight	356.98	473.13	348.11	468.20	235.11
T / K	100	100	100	100	100
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	*Iba*2	$P2_1/n$	*Ccc*2	$P2_1/n$	$P2_1/c$
a / Å	12.356(4)	8.647(5)	14.684(4)	13.3754(10)	9.8577(8)
b / Å	20.211(6)	14.863(7)	22.575(7)	11.0807(8)	10.3265(8)
c / Å	9.735(3)	15.435(8)	14.269(4)	13.7559(10)	13.5715(11)
β / deg		94.148(18)		102.726(3)	96.499(2)
V / Å^3	2431.2(12)	1978.5(17)	4730(2)	1988.7(3)	1372.64(19)
Z	8	4	16	4	4
$\rho_{calc.}$ / g cm^{-3}	1.951	1.588	1.9543	1.564	1.138
μ / mm^{-1}	0.216	0.161	0.216	0.150	0.068
F(000) / e	1376	944	2674.9	944	488
Refl. collected/unique	19274/2384	10659/3626	31184/4659	25500/4066	14304/2726
Refl. observed [$I > 2\sigma(I)$]	1862	2056	4010	3225	2385
R_{int}	0.0957	0.0801	0.0639	0.0492	0.0351
Restraints/parameters	4/227	0/294	0/426	0/300	0/217
θ range / deg	1.93–26.00	1.91–25.50	1.65–26.00	1.92–26.37	2.08–26.09
$R1$ [$I > 2\sigma(I)$][a]	0.0414	0.0740	0.0362	0.0375	0.0405
$wR2$ (all data)[b]	0.0869	0.1797	0.0957	0.0969	0.1249
GOF on F^2 [c]	1.309	1.175	1.0782	1.075	1.073
Larg. diff. peak/hole / e Å^{-3}	0.309/–0.413	0.492/–0.475	0.341/–0.243	0.263/–0.229	0.322/–0.197

[a] $R1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, weight scheme: $w = [\sigma^2 F_o + (aP)^2 + bP]^{-1}$; $P = [\max(0,F_o^2) + 2F_c^2]/3$; H**1**·$H_2O$: $a = 0.0031$, $b = 4.6387$; H**2**·diglyme: $a = 0.0169$, $b = 3.6200$; H**3**·0.5H_2O: $a = 0.0528$, $b = 0.5304$; [Et_4N]**1**: $a = 0.0455$, $b = 0.4087$; H**4**·$(CH_3)_2CO$: $a = 0.0815$, $b = 0.2877$; [c] GOF: $S = [\Sigma w(F_o^2 - F_c^2)^2/(m - n)]^{0.5}$; ($m$ = reflections, n = variables).

Table S2 Energies, enthalpies and free energies as well as free energies of solvation[a] calculated at the B3LYP/6-311++G(d,p) level of theory.

Compound	E^{ZPC} [au]	H [au]	G [au]	$G_S(H_2O)$ [kJ mol^{-1}] gas phase model	$G_S(H_2O)$ [kJ mol^{-1}] solute model[b]
[1-H-12-H_2N-*closo*-1-$CB_{11}F_{10}$]$^-$ (**1**)	–1367.570024	–1367.548691	–1367.615252	–204.1	–207.0
1-H-12-H_3N-*closo*-1-$CB_{11}F_{10}$ (H**1**)	–1368.032236	–1368.010643	–1368.079101	–135.4	–148.6
[1-H-7-H_2N-*closo*-1-$CB_{11}F_{10}$]$^-$ (**2**)	–1367.570586	–1367.549108	–1367.618334	–204.4	–209.3
1-H-7-H_3N-*closo*-1-$CB_{11}F_{10}$ (H**2**)	–1368.027809	–1368.006221	–1368.074760	–148.3	–169.9
[1-H-2-H_2N-*closo*-1-$CB_{11}F_{10}$]$^-$ (**3**)	–1367.572853	–1367.551667	–1367.617578	–206.3	–211.8
1-H-2-H_3N-*closo*-1-$CB_{11}F_{10}$ (H**3**)	–1368.014879	–1367.993338	–1368.060589	–179.3	–206.9

[a] G_S calculated using the conductor polarizable continuum model (CPCM). [b] The geometries were reoptimized within the CPCM.

Table S3 Experimental[a] and calculated[b] chemical shifts of **1**, H**1**, **2**, H**2**, **3** and H**3**.

Compound	^{1}H		^{13}C	^{11}B						^{19}F					
	$CH_{cluster}$	NH_n	$C_{cluster}$	B2–B6			B7–B11			B12	F2–F6	F7–F11			
[1-H-12-H_2N-*closo*-1-$CB_{11}F_{10}$]$^-$ (**1**)	3.36	≈ 1	15.9	–17.6			–15.3			–15.3	–256.1	–254.8			
calculated	1.80	–0.55	21.9	–19.3			–16.6			–16.1	–289.5	–288.1			
1-H-12-H_3N-*closo*-1-$CB_{11}F_{10}$ (H**1**)	4.14	6.49	22.5	–17.6			–16.0			–23.5	–250.8	–255.6			
calculated	2.70	3.60	31.6	–19.4			–18.5			–26.8	–275.5	–289.4			
	$CH_{cluster}$	NH_n	$C_{cluster}$	B2+B3	B4+B6	B5	B7	B8+B11	B9+B10	B12	F2+F3	F4+F6	F5	F8+F11	F9+F10	F12
[1-H-7-H_2N-*closo*-1-$CB_{11}F_{10}$]$^-$ (**2**)	3.27	n. o.[c]	18.0	–17.7	–17.4	–18.4	–22.5	–15.3	–16.2	–7.9	–257.3	–256.0	–257.4	–256.9	–256.3	–251.9
calculated	1.78	–0.47	23.8	–18.6	–18.9	–19.7	–24.3	–16.3	–17.1	–8.8	–291.5	–289.1	–290.1	–290.1	–287.8	–282.6
1-H-7-H_3N-*closo*-1-$CB_{11}F_{10}$ (H**2**)	3.88	6.61	19.6	–16.9	–16.9	–15.5	–31.4	–15.5	–15.5	–8.1	n.a.p.[d]	n.a.p.	–247.9	n.a.p.	n.a.p.	–251.1
calculated	2.48	3.61	25.4	–19.7	–18.4	–14.9	–33.7	–17.6	–16.8	–8.9	–292.3	–279.1	–267.7	–289.9	–275.3	–282.3
	$CH_{cluster}$	NH_n	$C_{cluster}$	B2	B3+B6	B4+B5	B7+B11	B8+B10	B9	B12	F3+F6	F4+F5	F7+F11	F8+F10	F9	F12
[1-H-2-H_2N-*closo*-1-$CB_{11}F_{10}$]$^-$ (**3**)	3.48	n. o.	18.7	–25.4	–17.8	–17.6	–15.2	–16.2	–15.6	–7.4	–257.4	–255.5	–256.0	–255.6	–255.0	–248.8
calculated	1.66	0.00	26.7	–26.3	–20.0	–18.9	–16.0	–17.6	–16.6	–8.0	–294.1	–289.5	–289.4	–287.9	–287.8	–277.4
1-H-2-H_3N-*closo*-1-$CB_{11}F_{10}$ (H**3**)	3.78	6.95	14.3	–32.0	–18.0	–17.1	–15.2	–15.9	–13.1	–6.9	–257.1	–252.9	–256.0	–253.1	–248.0	–245.0
calculated	1.89	3.90	17.4	–34.5	–20.9	–18.1	–17.0	–16.9	–11.5	–6.9	–294.3	–278.2	–289.9	–275.9	–261.7	–260.7

[a] Solvent: CD_3CN. [b] B3LYP/6-311++G(2d,p)//B3LYP/6-311++G(d,p). [c] n.o. = not observed. [d] n.a.p. = no assignment possible.

Table S4 Experimental and calculated[a] atomic distances[b] of 1-H-7-H_3N-*closo*-1-$CB_{11}F_{10}$ (H**2**), [1-H-7-H_2N-*closo*-1-$CB_{11}F_{10}$]$^-$ (**2**), 7-H_3N-12-F-*closo*-1-$CB_{11}H_{10}$ (H**4**), [7-H_2N-12-F-*closo*-1-$CB_{11}H_{10}$]$^-$ (**4**) and related {*closo*-1-CB_{11}} clusters.[c]

Compound/anion	**2**	H**2**·diglyme	H**2**	**4**	H**4**·H_2O	H**4**	[7-H_2N-*closo*-1-$CB_{11}H_{11}$]$^-$	7-H_3N-*closo*-1-$CB_{11}H_{11}$
	calc.	exp.	calc.	calc.	exp.	calc.	calc.	calc.
Ref.	[d]	[d]	[d]	1	[d]	1	1	1
d(B–N)	1.472	1.529(6)	1.562	1.493	1.546(2)	1.579	1.496	1.586
d(C–B2/B3)	1.718	1.717(8)	1.704	1.706	1.704(2)	1.698	1.702	1.697
d(C–B4/B6)	1.716	1.716(8)	1.736	1.706	1.715(2)	1.716	1.710	1.717
d(C–B5)	1.717	1.726(7)	1.728	1.704	1.714(2)	1.714	1.711	1.709
d(B2–B3)	1.788	1.803(8)	1.815	1.772	1.789(2)	1.797	1.786	1.796
d(B2–B6/B3–B4)	1.800	1.789(8)	1.792	1.779	1.776(2)	1.778	1.784	1.775
d(B5–B4/B6)	1.796	1.796(9)	1.808	1.784	1.785(2)	1.781	1.777	1.781
d(B2/B3–B7)	1.782	1.772(7)	1.752	1.788	1.760(2)	1.748	1.787	1.751
d(B2–B11/B3–B8)	1.772	1.778(7)	1.782	1.774	1.777(2)	1.779	1.768	1.782
d(B6–B11/B4–B8)	1.777	1.789(8)	1.775	1.768	1.772(2)	1.763	1.768	1.770
d(B6–B10/B4–B9)	1.779	1.788(8)	1.796	1.773	1.771(2)	1.780	1.769	1.780
d(B5–B9/B10)	1.779	1.774(8)	1.788	1.771	1.768(2)	1.775	1.776	1.777
d(B7–B8/B11)	1.823	1.798(8)	1.782	1.798	1.779(2)	1.761	1.814	1.759
d(B8–B9/B10–B11)	1.815	1.818(8)	1.814	1.794	1.787(2)	1.788	1.781	1.783
d(B9–B10)	1.817	1.794(9)	1.833	1.789	1.793(2)	1.800	1.792	1.796
d(B7–B12)	1.810	1.797(8)	1.775	1.813	1.772(2)	1.764	1.788	1.755
d(B8/B11–B12)	1.791	1.792(9)	1.808	1.783	1.787(2)	1.797	1.785	1.795
d(B9/B10–B12)	1.801	1.790(9)	1.794	1.780	1.779(2)	1.775	1.790	1.781
d(B2–F2/B3–F3)	1.367	1.361(6)	1.360	–	–	–	–	–
d(B4–F4/B6–F6)	1.366	1.359(7)	1.351	–	–	–	–	–
d(B5–F5)	1.366	1.363(7)	1.351	–	–	–	–	–
d(B8–F8/B11–F11)	1.376	1.365(7)	1.371	–	–	–	–	–
d(B9–F9/B10–F10)	1.373	1.377(6)	1.358	–	–	–	–	–
d(B12–F12)	1.378	1.367(7)	1.372	1.395	1.3865(15)	1.392	–	–

[a] B3LYP/6-311++G(d,p). [b] All *d*(CB), *d*(BB) and *d*(BF) distances are mean values for C_{5v} symmetry of the carborane cage; *d*(NH) are mean values. [c] Atomic distances in Å. [d] This work.

Table S5 Experimental and calculated[a] atomic distances[b] of 1-H-2-H_3N-*closo*-1-$CB_{11}F_{10}$ (H**3**), [1-H-2-H_2N-*closo*-1-$CB_{11}F_{10}$]$^-$ (**3**) and related {*closo*-1-CB_{11}} clusters.[c]

Compound/anion	**3**	H**3**·0.5H_2O	H**3**	[2-H_2N-*closo*-1-$CB_{11}H_{11}$]$^-$	2-H_3N-*closo*-1-$CB_{11}H_{11}$·EtOH	2-H_3N-*closo*-1-$CB_{11}H_{11}$
	calc.	exp.	calc.	calc.	exp.	calc.
Ref.	[d]	[d]	[d]	2	3	2
d(B–N)	1.460	1.530(4)	1.556	1.483	1.5396(10)	1.579
d(C–B2)	1.763	1.687(4)	1.671	1.744	1.6872(11)	1.672
d(C–B3/B6)	1.700	1.733(4)	1.729	1.699	1.7202(12)	1.723
d(C–B4/B5)	1.707	1.721(4)	1.724	1.701	1.7075(12)	1.710
d(B2–B3/B6)	1.793	1.788(4)	1.765	1.789	1.7697(12)	1.757
d(B3–B4/B5–B6)	1.803	1.804(4)	1.795	1.782	1.7782(12)	1.776
d(B4–B5)	1.788	1.807(4)	1.816	1.777	1.7885(13)	1.790
d(B2–B7/B11)	1.783	1.778(5)	1.756	1.785	1.7668(12)	1.744
d(B3–B7/B6–B11)	1.781	1.793(5)	1.789	1.774	1.7805(12)	1.783
d(B3–B8/B6–B10)	1.787	1.781(5)	1.778	1.774	1.7639(12)	1.767
d(B4–B8/B5–B10)	1.781	1.791(5)	1.793	1.776	1.7789(12)	1.781
d(B4/B5–B9)	1.779	1.790(5)	1.787	1.773	1.7731(12)	1.775
d(B7–B11)	1.795	1.811(4)	1.815	1.784	1.7985(12)	1.801
d(B7–B8/B10–B11)	1.806	1.809(4)	1.807	1.784	1.7876(12)	1.786
d(B9–B8/B10)	1.818	1.828(4)	1.829	1.792	1.7888(12)	1.791
d(B7/B11–B12)	1.803	1.803(4)	1.799	1.785	1.7799(12)	1.783
d(B8/B10–B12)	1.803	1.806(4)	1.823	1.784	1.7873(12)	1.792
d(B9–B12)	1.799	1.799(4)	1.811	1.783	1.7822(12)	1.784
d(B3–F3/B6–F6)	1.370	1.348(4)	1.366	–	–	–
d(B4–F4/B5–F5)	1.366	1.345(4)	1.352	–	–	–
d(B7–F7/B11–F11)	1.377	1.362(3)	1.371	–	–	–
d(B8–F8/B10–F10)	1.374	1.372(4)	1.358	–	–	–
d(B9–F9)	1.373	1.353(4)	1.357	–	–	–
d(B12–F12)	1.373	1.362(4)	1.358	–	–	–

[a] B3LYP/6-311++G(d,p). [b] All *d*(CB), *d*(BB) and *d*(BF) distances are mean values for C_{5v} symmetry of the carborane cage; *d*(NH) are mean values. [c] Atomic distances in Å. [d] This work.

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