Electronic Supplementary Information (ESI)

Probing the common alkali metals affinity of native and variously methylated β-cyclodextrins by combining electrospray-tandem mass spectrometry and molecular modeling

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- $E_0 = E_{elect}$ + ZPE Zero Point Energy at 0 K
- $E=E_0 + E_{trans} + E_{rot} + E_{vib}$ (thermal correction from 0 K to 298 K)

With : E_{elect} = Energy contributions from electronic motion
E_{trans} = Energy contributions from translation motion
E_{rot} = Energy contributions from rotational motion
E_{vib} = Energy contributions from vibrational motion
ZPE = zero-point energy as energy vibrational occuring even at 0 K

- Gibbs free energy : G=H-TS with thermal correction : H=E+RT

With : H = enthalpy (K)
R = ideal gas constant 1.9872041 $cal.K^{-1}.mol^{-1}$
T = temperature (K)
S = entropy ($cal.K^{-1}$)

Fig. S1 Main equations used for determining energy minimum.

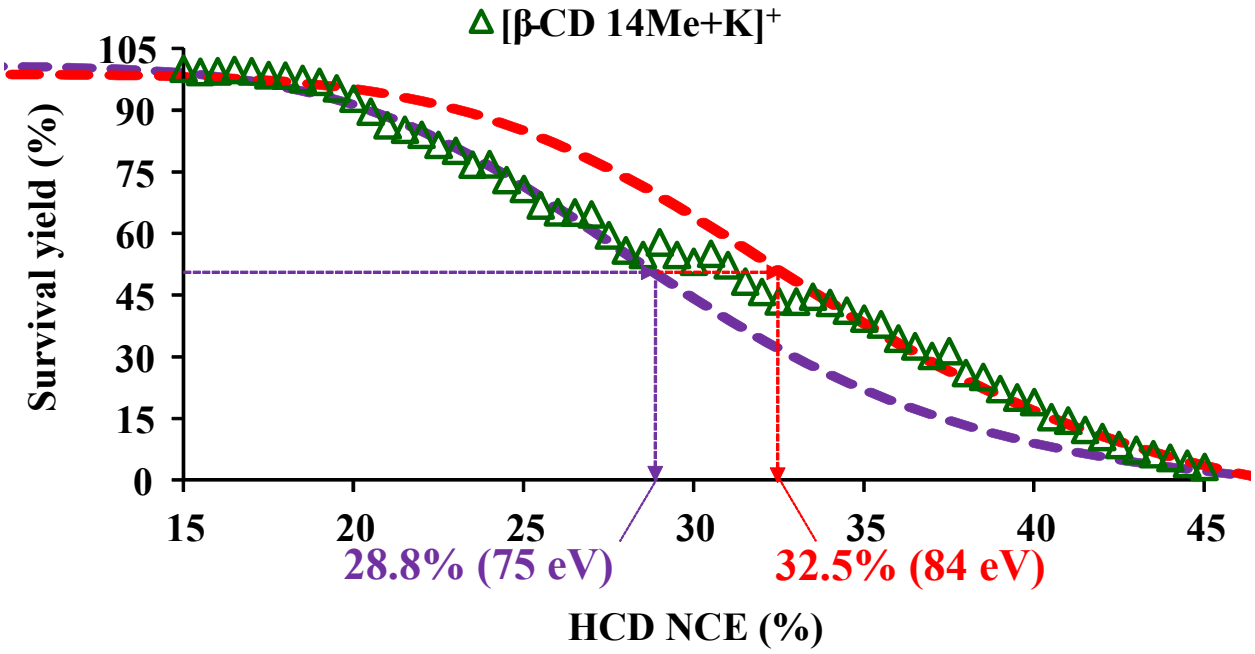

Fig. S2 Zoom between 15 and 45 % Normalized Collision Energy during Survival Yield experiment on monopotassied RAMEB (taking into account 14 methyl groups) upon HCD. We formulated hypothesis that curve obtained for this experiment (green triangle)(see Table 2 in article, not shown here) resulting in 30.2% (72 eV) as CE_{50} is an average of two sigmoid representing two region-isomers of dimethylated β-CD in the RAMEB : an homogeneous 2,6-O-methyl-β-CD (purple curve) and an heterogeneous of 2,3,6-O-methyl et 6-O-methyl glucose units (red curve) randomly distributed through the one β-CD molecule for a total of 14 methyl groups (red curve). Extrapolated CE_{50} values for $[M+K]^+$ led to 28.8% (75 eV), and 32.5% (84 eV), respectively.

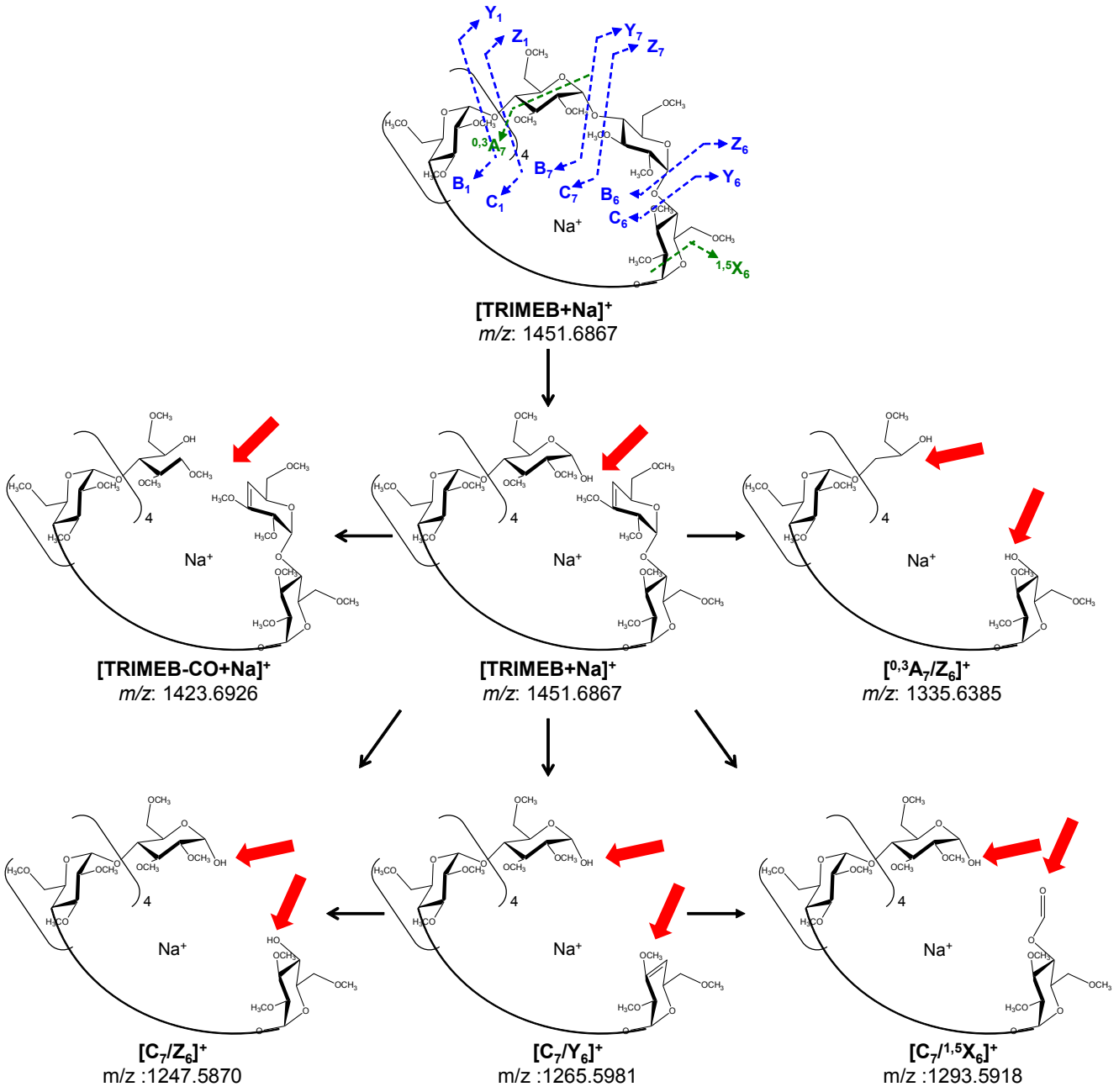

Figure S3. Example of fragmentation pathways for $[TRIMEB+Na]^+$ upon HCD.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}
cccc	0,13	0,17	0,08	0,08	0,35
cccw	2,91	2,27	2,48	2,48	2,37
cwcc	0,00	0,00	0,00	0,00	0,00
cwcw	2,71	1,85	2,21	2,21	1,56
o_cccc	20,28	17,33	18,91	18,91	12,40
o_cwcw	17,93	17,38	17,64	17,64	16,09

Table S1. Thermodynamic parameters for the six studied conformers of native β-CD.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}
cccc	15,38	14,83	15,11	15,11	12,91
cccw	13,75	14,30	13,76	13,76	16,75
cwcc	15,04	14,80	14,36	14,36	15,12
cwcw	12,78	13,64	13,01	13,01	16,08
o_cccc	14,35	13,30	14,00	14,00	9,87
o_cwcw	0,00	0,00	0,00	0,00	0,00

Table S2. Thermodynamic parameters for the six studied conformers of per-6-O-methyl β-CD (CRYSMEB).

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}
cccc	63,24	63,64	63,90	63,90	64,83
cccw	61,59	62,95	62,70	62,70	67,02
cwcc	11,64	11,99	11,94	11,94	13,34
cwcw	15,91	16,51	16,17	16,17	17,70
o_cccc	62,57	62,90	63,13	63,13	64,95
o_cwcw	0,00	0,00	0,00	0,00	0,00

Table S3. Thermodynamic parameters for the six studied conformers of per-3,6dimethyl β-CD (RAMEB).

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}
cccc	41,19	43,88	42,76	42,76	47,63
cccw	35,40	37,44	36,66	36,66	39,31
cwcc	9,72	9,84	10,09	10,09	9,86
cwcw	20,02	20,28	19,93	19,93	20,20
o_cccc	34,21	36,30	35,57	35,57	38,58
o_cwcw	0,00	0,00	0,00	0,00	0,00

Table S4. Thermodynamic parameters for the six studied conformers of per-2,3-6-trimethyl β-CD (TRIMEB).

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	7,13	7,23	7,05	7,05	7,70	7,61
cccw	6,07	6,65	6,18	6,18	7,54	8,04
cwcc	0,00	0,00	0,00	0,00	0,00	8,06
cwcw	2,71	3,84	3,52	3,52	4,23	8,04
o_cccc	20,28	14,42	15,10	15,10	12,46	7,41
o_cwcw	17,97	31,49	31,19	31,19	31,05	5,20

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-91,05 (+7,61)	-90,09 (+7,61)	-82,77 (+7,61)
cccw	-94,89 (+8,04)	-92,77 (+8,04)	-84,94 (+8,04)
cwcc	-98,05 (+8,06)	-97,15 (+8,06)	-90,12 (+8,06)
cwcw	-97,47 (+8,04)	-95,16 (+8,04)	-87,95 (+8,04)
o_cccc	-102,53 (+7,41)	-100,06 (+7,41)	-90,06 (+7,41)
o_cwcw	-84,90 (+5,20)	-83,04 (+5,20)	-75,15 (+5,20)

Table S5. Thermodynamic parameters for the six studied conformers of native β-CD interacting with one lithium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	5,59	5,54	5,42	5,42	5,83	8,33
cccw	7,85	7,86	7,69	7,69	8,24	8,46
cwcc	0,00	0,00	0,00	0,00	0,00	8,97
cwcw	5,52	5,34	5,36	5,36	5,18	8,48
o_cccc	13,76	12,24	12,96	12,96	9,86	8,00
o_cwcw	16,00	16,08	15,99	15,99	15,05	7,23

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-67,25 (+8,33)	-67,53 (+8,33)	-60,40 (+8,33)
cccw	-67,78 (+8,46)	-67,30 (+8,46)	-60,01 (+8,46)
cwcc	-72,72 (+8,97)	-72,89 (+8,97)	-65,88 (+8,97)
cwcw	-69,90 (+8,48)	-69,40 (+8,48)	-62,27 (+8,48)
o_cccc	-79,24 (+8,00)	-77,98 (+8,00)	-68,42 (+8,00)
o_cwcw	-74,69 (+7,23)	-74,19 (+7,23)	-66,92 (+7,23)

Table S6. Thermodynamic parameters for the six studied conformers of native β-CD interacting with one sodium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	4,29	4,38	4,22	4,22	4,98	7,82
cccw	6,24	6,31	6,16	6,16	6,79	7,96
cwcc	0,00	0,00	0,00	0,00	0,00	8,79
cwcw	3,85	3,98	3,92	3,92	4,18	8,02
o_cccc	2,19	2,03	2,07	2,07	2,77	8,74
o_cwcw	13,26	14,19	13,70	13,70	15,15	6,10

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-45,86 (+7,82)	-46,75 (+7,82)	-40,55 (+7,82)
cccw	-46,69 (+7,96)	-46,92 (+7,96)	-40,75 (+7,96)
cwcc	-50,02 (+8,79)	-50,96 (+8,79)	-45,17 (+8,79)
cwcw	-48,87 (+8,02)	-48,83 (+8,02)	-42,55 (+8,02)
o_cccc	-68,12 (+8,74)	-66,26 (+8,74)	-54,80 (+8,74)
o_cwcw	-54,74 (+6,10)	-54,15 (+6,10)	-46,11 (+6,10)

Table S7. Thermodynamic parameters for the six studied conformers of native β-CD interacting with one potassium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	4,24	3,58	3,22	3,22	3,75	6,33
cccw	29,66	29,46	28,89	28,89	30,28	5,47
cwcc	0,66	1,17	1,06	1,06	1,51	6,14
cwcw	34,07	33,55	33,17	33,17	33,15	5,39
o_cccc	0,00	0,00	0,00	0,00	0,00	6,20
o_cwcw	4,56	4,97	4,83	4,83	6,40	6,14

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-106,33 (+6,33)	-104,25 (+6,33)	-93,13 (+6,33)
cccw	-79,28 (+5,47)	-77,84 (+5,47)	-70,45 (+5,47)
cwcc	-109,57 (+6,14)	-106,63 (+6,14)	-97,59 (+6,14)
cwcw	-73,90 (+5,39)	-73,08 (+5,39)	-66,90 (+5,39)
o_cccc	-109,54 (+6,20)	-106,30 (+6,20)	-93,84 (+6,20)
o_cwcw	-90,63 (+6,14)	-88,03 (+6,14)	-77,58 (+6,14)

Table S8. Thermodynamic parameters for the six studied conformers of per-6-O-methyl β-CD (CRYSMEB) interacting with one lithium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	8,90	8,53	8,58	8,58	7,11	6,99
cccw	29,90	29,73	29,16	29,16	29,84	6,14
cwcc	0,59	0,85	0,77	0,77	1,12	7,07
cwcw	26,84	26,66	26,24	26,24	26,52	6,06
o_cccc	0,00	0,00	0,00	0,00	0,00	7,16
o_cwcw	5,16	4,90	5,04	5,04	4,51	7,39

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-80,81 (+6,99)	-79,34 (+6,99)	-69,11 (+6,99)
cccw	-58,18 (+6,14)	-57,61 (+6,14)	-50,23 (+6,14)
cwcc	-88,78 (+7,07)	-87,00 (+7,07)	-77,32 (+7,07)
cwcw	-60,26 (+6,06)	-60,03 (+6,06)	-52,88 (+6,06)
o_cccc	-88,68 (+7,16)	-86,35 (+7,16)	-73,19 (+7,16)
o_cwcw	-69,17 (+7,39)	-68,15 (+7,39)	-58,81 (+7,39)

Table S9. Thermodynamic parameters for the six studied conformers of per-6-O-methyl β-CD (CRYSMEB) interacting with one sodium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	2,76	2,82	2,83	2,83	2,46	8,27
cccw	27,21	27,22	26,55	26,55	27,53	5,88
cwcc	0,86	1,37	1,18	1,18	1,30	7,29
cwcw	20,09	20,62	20,04	20,04	21,88	6,90
o_cccc	0,65	1,14	0,88	0,88	1,35	7,42
o_cwcw	0,00	0,00	0,00	0,00	0,00	8,00

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-65,30 (+8,27)	-64,24 (+8,27)	-53,69 (+8,27)
cccw	-39,23 (+5,88)	-39,30 (+5,88)	-32,47 (+5,88)
cwcc	-66,85 (+7,29)	-65,66 (+7,29)	-57,07(+7,29)
cwcw	-45,37 (+6,90)	-45,25 (+6,90)	-37,44 (+6,90)
o_cccc	-66,38 (+7,42)	-64,39 (+7,42)	-51,76 (+7,42)
o_cwcw	-52,68 (+8,00)	-52,23 (+8,00)	-43,24 (+8,00)

Table S10. Thermodynamic parameters for the six studied conformers of per-6-O-methyl β-CD (CRYSMEB) interacting with one potassium Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	52,22	52,22	52,45	52,45	54,00	4,47
cccw	69,03	68,38	68,79	68,79	69,36	6,37
cwcc	0,00	0,00	0,00	0,00	0,00	5,59
cwcw	15,21	14,75	14,57	14,57	15,36	6,12
o_cccc	53,09	53,24	53,48	53,48	55,11	5,76
o_cwcw	13,79	13,19	13,28	13,28	13,12	6,12

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-111,10 (+4,47)	-108,20 (+4,47)	-97,76 (+4,47)
cccw	-92,65 (+6,37)	-91,34 (+6,37)	-84,60 (+6,37)
cwcc	-111,73 (+5,59)	-108,77 (+5,59)	-100,27 (+5,59)
cwcw	-100,78 (+6,12)	-98,53 (+6,12)	-89,28 (+6,12)
o_cccc	-109,57 (+5,76)	-106,44 (+5,76)	-96,77 (+5,76)
o_cwcw	-86,30 (+6,12)	-83,58 (+6,12)	-73,82 (+6,12)

Table S11. Thermodynamic parameters for the six studied conformers of per-3,6-O-dimethyl β-CD (RAMEB) interacting with one lithium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	51,04	50,89	51,20	51,20	51,85	6,58
cccw	53,63	53,26	53,52	53,52	54,73	7,32
cwcc	0,00	0,00	0,00	0,00	0,00	6,90
cwcw	20,36	19,91	19,71	19,71	19,92	6,13
o_cccc	50,12	50,20	50,49	50,49	51,76	6,83
o_cwcw	11,61	11,15	11,21	11,21	10,07	6,45

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-90,02 (+6,58)	-88,40 (+6,58)	-77,91 (+6,58)
cccw	-85,78 (+7,32)	-85,34 (+7,32)	-77,21 (+7,32)
cwcc	-89,46 (+6,90)	-87,64 (+6,90)	-78,26 (+6,90)
cwcw	-73,36 (+6,13)	-72,25 (+6,13)	-62,71 (+6,13)
o_cccc	-90,26 (+6,83)	-88,35 (+6,83)	-78,11 (+6,83)
o_cwcw	-66,21 (+6,45)	-64,50 (+6,45)	-54,85 (+6,45)

Table S12. Thermodynamic parameters for the six studied conformers of per-3,6-O-dimethyl β-CD (RAMEB) interacting with one sodium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	58,20	58,59	58,80	58,80	59,68	7,39
cccw	57,25	56,29	56,91	56,91	55,83	8,72
cwcc	0,00	0,00	0,00	0,00	0,00	7,85
cwcw	24,89	24,94	24,75	24,75	24,87	5,91
o_cccc	57,03	57,61	57,88	57,88	59,26	7,25
o_cwcw	5,75	6,23	5,92	5,92	7,73	7,34

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-67,41 (+7,39)	-88,40 (+7,39)	-77,91 (+7,39)
cccw	-66,72 (+8,72)	-85,34 (+8,72)	-77,21 (+8,72)
cwcc	-74,01 (+7,85)	-87,64 (+7,85)	-78,26 (+7,85)
cwcw	-53,39 (+5,91)	-72,25 (+5,91)	-62,71 (+5,91)
o_cccc	-67,90 (+7,25)	-88,35 (+7,25)	-78,11 (+7,25)
o_cwcw	-56,62 (+7,34)	-64,50 (+7,34)	-54,85 (+7,34)

Table S13. Thermodynamic parameters for the six studied conformers of per-3,6-O-dimethyl β-CD (RAMEB) interacting with one potassium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	36,77	37,83	37,72	37,72	37,33	5,55
cccw	48,01	49,26	48,76	48,76	50,40	5,58
cwcc	9,03	8,17	8,81	8,81	6,84	4,72
cwcw	23,90	23,09	23,30	23,30	22,06	5,13
o_cccc	38,15	39,22	39,14	39,14	38,33	5,87
o_cwcw	0,00	0,00	0,00	0,00	0,00	6,32

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-115,27 (+5,55)	-113,33 (+5,55)	-107,14 (+5,55)
cccw	-98,34 (+5,58)	-95,45 (+5,58)	-85,75 (+5,58)
cwcc	-111,61 (+4,72)	-108,95 (+4,72)	-99,86 (+4,72)
cwcw	-106,99 (+5,13)	-104,47 (+5,13)	-94,99 (+5,13)
o_cccc	-106,95 (+5,87)	-104,36 (+5,87)	-97,08 (+5,87)
o_cwcw	-110,89 (+6,32)	-107,28 (+6,32)	-96,84 (+6,32)

Table S14. Thermodynamic parameters for the six studied conformers of per-2,3,6-O-dimethyl β-CD (TRIMEB) interacting with one lithium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	33,73	36,00	35,33	35,33	38,39	6,75
cccw	41,26	42,99	42,27	42,27	45,00	6,81
cwcc	5,40	5,34	5,64	5,64	4,93	6,51
cwcw	7,64	7,79	7,87	7,87	7,34	7,89
o_cccc	34,58	36,83	36,30	36,30	39,10	6,70
o_cwcw	0,00	0,00	0,00	0,00	0,00	7,56

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-95,11 (+6,75)	-93,46 (+6,75)	-84,31 (+6,75)
cccw	-81,88 (+6,81)	-80,03 (+6,81)	-69,37 (+6,81)
cwcc	-92,03 (+6,51)	-90,08 (+6,51)	-80,00 (+6,51)
cwcw	-100,04 (+7,89)	-98,08 (+7,89)	-87,93 (+7,89)
o_cccc	-87,31 (+6,70)	-85,05 (+6,70)	-74,54 (+6,70)
o_cwcw	-87,68 (+7,56)	-85,58 (+7,56)	-75,06 (+7,56)

Table S15. Thermodynamic parameters for the six studied conformers of per-2,3,6-O-dimethyl β-CD (TRIMEB) interacting with one sodium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	34,61	36,95	36,16	36,16	39,12	7,20
cccw	43,27	44,99	44,25	44,25	46,72	7,58
cwcc	7,74	6,93	7,56	7,56	5,25	7,19
cwcw	0,00	0,00	0,00	0,00	0,00	8,52
o_cccc	35,71	38,14	37,37	37,37	40,96	7,14
o_cwcw	5,68	5,07	5,24	5,24	3,88	7,89

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-75,19 (+7,20)	-73,99 (+7,20)	-65,59 (+7,20)
cccw	-60,84 (+7,58)	-59,50 (+7,58)	-49,68 (+7,58)
cwcc	-70,66 (+7,19)	-69,97 (+7,19)	-61,70 (+7,19)
cwcw	-88,65 (+8,52)	-87,34 (+8,52)	-77,29 (+8,52)
o_cccc	-67,15 (+7,14)	-65,21 (+7,14)	-54,70 (+7,14)
o_cwcw	-62,97 (+7,89)	-61,99 (+7,89)	-53,21 (+7,89)

Table S16. Thermodynamic parameters for the six studied conformers of per-2,3,6-O-dimethyl β-CD (TRIMEB) interacting with one potassium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	2,40	1,35	1,70	1,70	0,32	15,70
cccw	2,68	2,56	2,57	2,57	2,04	15,60
cwcc	22,74	21,81	22,09	22,09	21,54	14,94
cwcw	7,98	6,91	7,31	7,31	5,52	13,32
o_cccc	0,59	0,00	0,20	0,20	0,00	14,62
o_cwcw	0,00	0,38	0,00	0,00	1,10	14,62

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-138,44 (+15,70)	-137,26 (+15,70)	-124,31 (+15,70)
cccw	-140,94 (+15,60)	-138,15 (+15,60)	-124,61 (+15,60)
cwcc	-117,97 (+14,94)	-116,63 (+14,94)	-102,75 (+14,94)
cwcw	-135,43 (+13,32)	-133,38 (+13,32)	-120,33 (+13,32)
o_cccc	-160,40 (+14,62)	-155,76 (+14,62)	-136,69 (+14,62)
o_cwcw	-158,68 (+14,62)	-155,43 (+14,62)	-139,27 (+14,62)

Table S17. Thermodynamic parameters for the six studied conformers of native β-CD interacting with two lithium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	3,70	3,58	3,59	3,59	2,95	15,93
cccw	3,20	3,94	3,60	3,60	4,03	15,26
cwcc	19,68	19,59	19,59	19,59	19,66	15,77
cwcw	6,72	6,44	6,59	6,59	5,20	13,11
o_cccc	0,00	0,00	0,00	0,00	0,00	14,90
o_cwcw	0,63	1,36	0,90	0,90	1,75	14,52

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-112,34 (+15,93)	-111,91(+15,93)	-98,71 (+15,93)
cccw	-115,63 (+15,26)	-113,64 (+15,26)	-99,64 (+15,26)
cwcc	-96,24 (+15,77)	-95,73 (+15,77)	-81,65 (+15,77)
cwcw	-111,89 (+13,11)	-110,72 (+13,11)	-97,67 (+13,11)
o_cccc	-136,20 (+14,90)	-132,64 (+14,90)	-113,71 (+14,90)
o_cwcw	-133,26 (+14,52)	-131,33 (+14,52)	-115,65 (+14,52)

Table S18. Thermodynamic parameters for the six studied conformers of native β-CD interacting with one lithium and one sodium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	73,78	75,91	75,22	75,22	78,68	10,20
cccw	65,81	66,40	66,00	66,00	66,06	12,60
cwcc	21,38	21,47	21,63	21,63	22,28	10,66
cwcw	20,10	19,12	19,43	19,43	18,61	12,34
o_cccc	76,62	78,60	77,74	77,74	82,36	10,24
o_cwcw	0,00	0,00	0,00	0,00	0,00	11,75

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-154,52 (+10,20)	-129,19 (+10,20)	-111,17 (+10,20)
cccw	-156,80 (+12,60)	-121,31 (+12,60)	-106,53 (+12,60)
cwcc	-175,52 (+10,66)	-164,02 (+10,66)	-145,17 (+10,66)
cwcw	-187,04 (+12,34)	-160,89 (+12,34)	-144,05 (+12,34)
o_cccc	-144,74 (+10,24)	-156,85 (+10,24)	-140,44 (+10,24)
o_cwcw	-187,14 (+11,75)	-151,55 (+11,75)	-134,31 (+11,75)

Table S19. Thermodynamic parameters for the six studied conformers of per-2,3,6-O-dimethyl β-CD (TRIMEB) interacting with two lithium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.

Conformation	$\Delta E_{élect}$ kcal.mol^{-1}	ΔE_0 kcal.mol^{-1}	ΔE kcal.mol^{-1}	ΔH kcal.mol^{-1}	ΔG kcal.mol^{-1}	BSSE
cccc	71,03	73,34	72,56	72,56	76,26	11,84
cccw	69,79	70,62	70,16	70,16	70,06	13,34
cwcc	15,32	15,35	15,61	15,61	15,81	12,30
cwcw	10,50	10,23	10,27	10,27	10,84	14,11
o_cccc	52,85	54,68	53,85	53,85	57,81	12,04
o_cwcw	0,00	0,00	0,00	0,00	0,00	13,47

Conformation	E^{elect}_{int} kcal.mol^{-1}	E^0_{int} kcal.mol^{-1}	ΔG_{int} kcal.mol^{-1}
cccc	-132,71 (+11,84)	-128,55 (+11,84)	-111,05 (+11,84)
cccw	-128,25 (+13,34)	-124,83 (+13,34)	-108,92 (+13,34)
cwcc	-157,02 (+12,30)	-152,50 (+12,30)	-133,72 (+12,30)
cwcw	-172,09 (+14,11)	-168,06 (+14,11)	-149,04 (+14,11)
o_cccc	-143,94 (+12,04)	-139,63 (+12,04)	-120,44 (+12,04)
o_cwcw	-162,58 (+13,47)	-158,02 (+13,47)	-139,68 (+13,47)

Table S20. Thermodynamic parameters for the six studied conformers of per-2,3,6-O-dimethyl β-CD (TRIMEB) interacting with one lithium and one sodium**.** Basis Set Superposition Errors (BSSE) was indicated in brackets.