Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic supplementary information

Approximate quantum chemical methods for modelling carbohydrate conformation and aromatic interactions: *β*-cyclodextrin and its adsorption on a single-layer graphene sheet

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Figure S1 View of βCD facing into the C2C3 rim

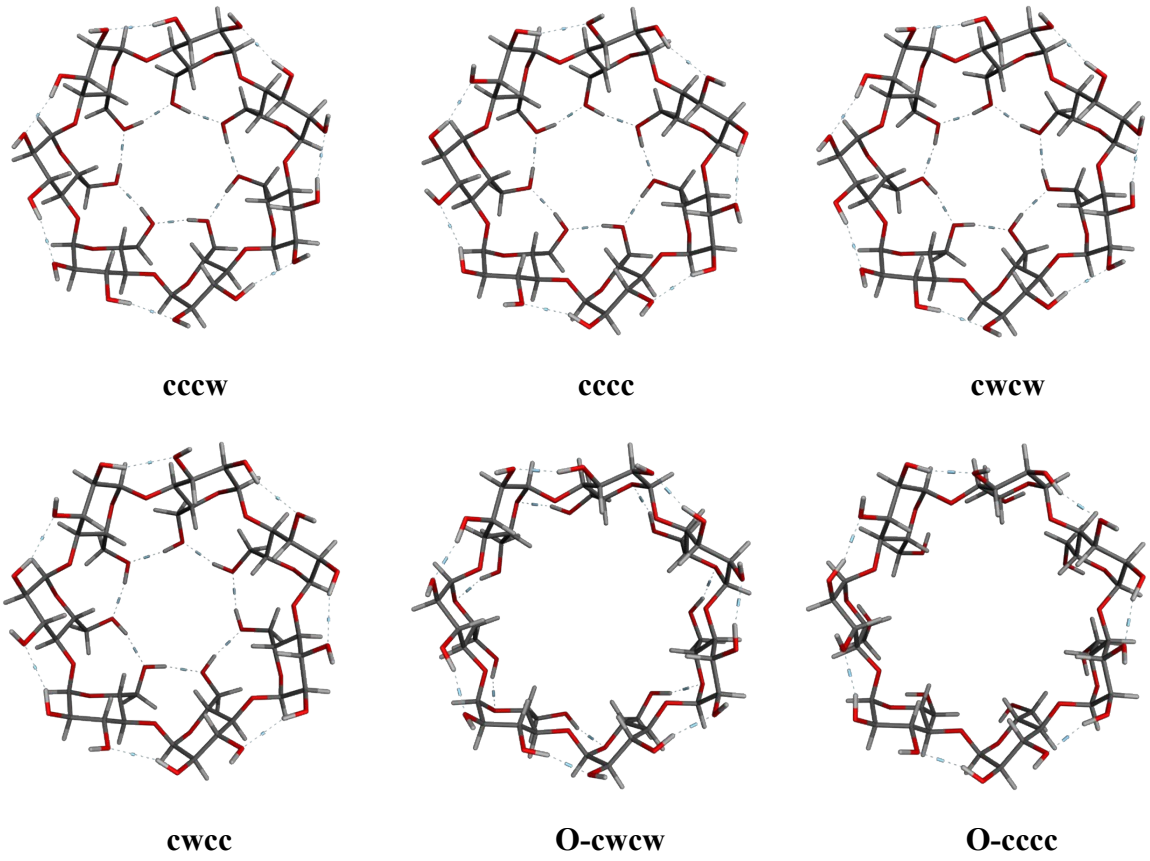

Table S1 Geometrical data for *β*CD structures optimised at the M06-2X/def2-TZVPP level of theory. Angles are mean values (averaged over glucosyl residue) in degrees. Standard errors of mean in parentheses.

Coordinate	cccw	cccc	cwcw	cwcc	O-cwcw	O-cccc	X-ray[a]
α (O4O4'O4'')	128.6 (0.31)	128.5 (0.62)	128.6 (0.10)	128.6 (0.19)	128.6 (0.14)	128.5 (0.17)	128±2
θ (C1O4'C4')	118.9 (0.05)	119.1 (0.12)	118.7 (0.03)	118.9 (0.04)	119.9 (0.03)	119.5 (0.06)	118±1
Φ (C2C1O4'C4')	221.8 (0.52)	222.2 (1.00)	220.8 (0.27)	221.3 (0.35)	232.9 (0.50)	232.6 (2.66)	231±6
τ (O4O4'O4''O4''')	0.0 (0.42)	0.0 (1.20)	0.0 (0.31)	0.0 (0.54)	0.0 (0.86)	0.0 (2.70)	0.2±9
Γ (C1C2C3C4)	308.6 (0.09)	307.4 (0.13)	308.9 (0.05)	307.6 (0.05)	305.4 (0.07)	304.0 (0.20)	306±3
Θ (C2C3C4C5)	55.0 (0.04)	56.4 (0.12)	55.0 (0.05)	56.4 (0.07)	53.2 (0.15)	55.1 (0.15)	55±3
Τ (C3C4C5O5)	300.4 (0.17)	300.2 (0.37)	300.3 (0.06)	300.1 (0.11)	306.3 (0.27)	305.4 (0.26)	304±4
ϑ (O4C4C5O5)	183.0 (0.26)	182.2 (0.57)	183.5 (0.09)	182.6 (0.15)	188.2 (0.24)	186.5 (0.31)	188±4
Ζ (O4C4C5C6)	62.4 (0.33)	61.5 (0.66)	63.2 (0.12)	62.2 (0.20)	71.6 (0.33)	68.5 (0.29)	69±5
Λ (O4'C1O5C5)	57.9 (0.20)	57.9 (0.38)	58.2 (0.04)	58.1 (0.07)	59.6 (0.14)	59.2 (0.07)	59±2
Π (C4C5O5C1)	65.2 (0.21)	64.1 (0.43)	65.6 (0.06)	64.6 (0.08)	60.5 (0.16)	59.0 (0.26)	59±3
Κ (O2C2C1O5)	176.8 (0.05)	178.1 (0.06)	176.2 (0.03)	177.4 (0.05)	179.3 (0.07)	181.1 (0.19)	178±3
Υ (O3C3C4C5)	126.1 (0.06)	177.1 (0.08)	126.3 (0.05)	177.3 (0.06)	122.7 (0.13)	174.9 (0.24)	176±2
Ε (O4'C1C4C5)	288.2 (0.11)	287.0 (0.23)	288.7 (0.04)	287.5 (0.08)	284.9 (0.18)	282.9 (0.30)	285±3

Ω (O5C5C6O6)	118.9 (1.26)	118.1 (2.42)	96.9 (0.49)	96.3 (0.66)	167.8 (0.69)	59.2 (0.45)	198±123
Ξ (C4C5C6O6)	238.9 (1.25)	238.7 (2.37)	216.8 (0.50)	216.7 (0.67)	286.8 (0.69)	179.5 0.01	112±70
ψ (O2C2C3O3)	65.6 (0.08)	62.4 (0.15)	65.7 (0.04)	62.5 (0.04)	61.5 (0.11)	58.9 (0.22)	63.6±2.1

[a]X-ray diffraction data from T. Heine, H. F. Dos Santos, S. Patchkovskii and H. A. Duarte, *J. Phys. Chem. A*, 2007, **111**, 5648-5654; K. Lindner and W. Saenger, *Carbohydr. Res.*, 1982, **99**, 103-115.

Table S2 Intramolecular interresidue hydrogen bond distances (in Å) at C2C3 rim of *β*CD geometries optimised at different levels of theory. For (O-)xxcw conformers, these distances are for O3-H···O2′; for (O-)xxcc conformers, these distances are for O3···H-O2′.

*β*CD	M06-2X/def2-TZVPP								DFTB3							
	glu1	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**	**glu1**	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**
cccw	2.11	2.09	2.13	2.11	2.08	2.12	2.13	**2.11**	2.03	2.03	2.03	2.03	2.03	2.03	2.03	**2.03**
cccc	2.14	2.15	2.09	2.11	2.17	2.09	2.13	**2.12**	2.04	2.03	2.04	2.04	2.04	2.04	2.03	**2.04**
cwcw	2.13	2.12	2.14	2.12	2.13	2.14	2.14	**2.13**	2.04	2.04	2.04	2.04	2.04	2.04	2.04	**2.04**
cwcc	2.15	2.15	2.14	2.13	2.15	2.13	2.14	**2.14**	2.05	2.05	2.05	2.05	2.05	2.04	2.05	**2.05**
O-cwcw	1.90	1.87	1.88	1.89	1.89	1.88	1.87	**1.88**	1.82	1.82	1.82	1.82	1.82	1.82	1.82	**1.82**
O-cccc	1.96	1.92	1.93	1.95	1.92	1.96	1.92	**1.94**	1.83	1.83	1.84	1.86	1.85	1.83	1.80	**1.83**
*β*CD	PM7								PM6-DH2							
	glu1	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**	**glu1**	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**
cccw	2.07	2.07	2.07	2.07	2.07	2.07	2.07	**2.07**	1.88	1.89	1.89	1.88	1.89	1.89	1.89	**1.89**
cccc	2.06	2.06	2.05	2.06	2.06	2.05	2.05	**2.06**	1.89	1.89	1.89	1.89	1.89	1.89	1.89	**1.89**
cwcw	2.08	2.08	2.08	2.07	2.08	2.08	2.07	**2.08**	1.89	1.89	1.89	1.89	1.89	1.89	1.89	**1.89**
cwcc	2.06	2.06	2.06	2.06	2.06	2.06	2.06	**2.06**	1.90	1.89	1.89	1.90	1.90	1.89	1.89	**1.89**
O-cwcw	1.71	1.70	1.70	1.70	1.70	1.70	1.70	**1.70**	1.79	1.78	1.79	1.79	1.78	1.78	1.79	**1.78**
O-cccc[a]	*1.73*	*1.73*	*1.73*	*1.73*	*1.73*	*1.73*	*1.73*	***1.73***	*1.89*	*1.89*	*1.89*	*1.90*	*1.88*	*1.95*	*1.96*	***1.91***
*β*CD	PM6-D3								PM6							
	glu1	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**	**glu1**	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**
cccw	1.91	1.91	1.92	1.91	1.91	1.91	1.92	**1.91**	2.02	2.02	2.02	2.02	2.02	2.02	2.02	**2.02**
cccc	1.94	1.94	1.93	1.94	1.95	1.93	1.93	**1.94**	2.04	2.04	2.03	2.04	2.04	2.03	2.03	**2.04**
cwcw	1.91	1.91	1.91	1.91	1.91	1.91	1.91	**1.91**	2.03	2.03	2.03	2.03	2.03	2.03	2.03	**2.03**
cwcc	1.94	1.94	1.93	1.93	1.94	1.93	1.93	**1.93**	2.05	2.04	2.04	2.04	2.04	2.04	2.04	**2.04**
O-cwcw	1.77	1.77	1.77	1.77	1.77	1.77	1.77	**1.77**	1.84	1.83	1.84	1.84	1.83	1.83	1.83	**1.83**
O-cccc[a]	*1.94*	*1.93*	*1.94*	*1.97*	*1.94*	*1.93*	*1.95*	***1.94***	*2.05*	*2.03*	*2.05*	*2.07*	*2.04*	*2.03*	*2.06*	***2.05***
*β*CD	PM3CARB-1								PM3-D*							
	glu1	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**	**glu1**	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**
cccw	1.93	1.93	1.93	1.93	1.93	1.93	1.93	**1.93**	1.86	1.86	2.62	2.43	1.85	2.61	2.44	**2.24**

cccc	1.89	1.89	1.89	1.89	1.89	1.89	1.89	**1.89**	2.53	2.68	1.86	2.61	2.70	1.86	2.59	**2.40**
cwcw	1.92	1.92	1.92	1.92	1.92	1.92	1.92	**1.92**	2.40	2.40	2.40	2.40	2.40	2.40	2.40	**2.40**
cwcc	1.89	1.89	1.89	1.89	1.88	1.89	1.89	**1.89**	2.52	2.52	2.52	2.52	2.52	2.52	2.52	**2.52**
O-cwcw	1.83	1.83	1.83	1.83	1.83	1.83	1.83	**1.83**	1.81	1.81	1.81	1.81	1.81	1.81	1.81	**1.81**
O-cccc	1.84	1.84	1.84	1.84	1.84	1.84	1.84	**1.84**	1.81	1.81	1.81	1.81	1.81	1.81	1.81	**1.81**
βCD	**PM3**								**AM1**							
	glu1	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**	**glu1**	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**
cccw	1.87	1.86	2.60	1.87	1.87	1.86	2.60	**2.08**	2.13	2.14	2.13	2.13	2.14	2.14	2.13	**2.13**
cccc	2.52	2.68	1.86	2.60	2.69	1.86	2.57	**2.40**	2.16	2.16	2.15	2.16	2.16	2.16	2.15	**2.16**
cwcw	1.86	1.86	2.60	1.87	1.86	2.58	2.42	**2.15**	2.14	2.14	2.13	2.13	2.14	2.14	2.13	**2.14**
cwcc	2.52	2.51	2.51	2.51	2.52	2.51	2.51	**2.51**	2.17	2.16	2.16	2.16	2.16	2.16	2.16	**2.16**
O-cwcw	1.81	1.81	1.81	1.81	1.81	1.81	1.81	**1.81**	2.15	2.15	2.14	2.14	2.14	2.13	2.14	**2.14**
O-cccc[a]	*1.81*	*1.81*	*1.81*	*1.81*	*1.81*	*1.81*	*1.81*	***1.81***	*2.18*	*2.16*	*2.17*	*2.18*	*2.14*	*2.19*	*2.16*	***2.17***

[a]Collapsed open structure labelled in *italics*

Table S3 Intramolecular interresidue hydrogen bond distances (in Å) at C6 rim of *β*CD geometries optimised at different levels of theory. For cwxx conformers, these distances are for O6-H···O6′; for ccxx conformers, these distances are for O6···H-O6′. For the O-cwcw, these distances are for O6-H···O5′; for O-cccc, no interresidue hydrogen bonds were present at the C6 rim.

***β*CD**	**M06-2X/def2-TZVPP**								**DFTB3**							
	glu1	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**	**glu1**	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**
cccw	1.82	1.83	1.83	1.84	1.83	1.82	1.83	**1.83**	1.80	1.80	1.80	1.80	1.80	1.80	1.80	**1.80**
cccc	1.83	1.84	1.84	1.85	1.85	1.83	1.84	**1.84**	1.80	1.80	1.80	1.80	1.80	1.80	1.80	**1.80**
cwcw	1.86	1.87	1.88	1.87	1.87	1.88	1.87	**1.87**	1.80	1.80	1.80	1.80	1.80	1.80	1.80	**1.80**
cwcc	1.86	1.88	1.89	1.87	1.88	1.89	1.88	**1.88**	1.79	1.79	1.79	1.79	1.79	1.79	1.79	**1.79**
O-cwcw	1.90	1.92	1.90	1.90	1.90	1.91	1.91	**1.90**	1.92	1.92	1.92	1.92	1.92	1.92	1.92	**1.92**
O-cccc	3.91	3.90	3.89	3.79	3.90	3.98	4.02	**3.91**	4.80	4.67	4.90	4.25	4.42	4.91	5.43	**4.77**
***β*CD**	**PM7**								**PM6-DH2**							
	glu1	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**	**glu1**	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**
cccw	1.70	1.70	1.70	1.70	1.70	1.70	1.70	**1.70**	1.79	1.79	1.79	1.79	1.79	1.79	1.79	**1.79**
cccc	1.70	1.70	1.70	1.70	1.70	1.70	1.70	**1.70**	1.79	1.80	1.79	1.79	1.80	1.79	1.79	**1.79**
cwcw	1.70	1.70	1.70	1.70	1.70	1.70	1.70	**1.70**	1.79	1.79	1.79	1.79	1.79	1.79	1.79	**1.79**
cwcc	1.70	1.70	1.70	1.70	1.70	1.70	1.70	**1.70**	1.79	1.79	1.79	1.79	1.79	1.79	1.79	**1.79**
O-cwcw	1.73	1.73	1.73	1.73	1.73	1.73	1.73	**1.73**	1.94	1.95	1.94	1.94	1.95	1.95	1.94	**1.94**
O-cccc[a]	*2.05*	*2.05*	*2.06*	*2.06*	*2.05*	*2.05*	*2.06*	***2.05***	*1.77*	*1.79*	*1.81*	*1.80*	*1.78*	*1.77*	*1.78*	***1.78***
***β*CD**	**PM6-D3**								**PM6**							
	glu1	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**	**glu1**	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**
cccw	1.77	1.77	1.77	1.77	1.77	1.77	1.77	**1.77**	1.86	1.86	1.86	1.86	1.86	1.86	1.86	**1.86**
cccc	1.78	1.78	1.77	1.78	1.77	1.77	1.77	**1.77**	1.87	1.87	1.86	1.87	1.87	1.87	1.87	**1.87**
cwcw	1.75	1.76	1.76	1.75	1.75	1.76	1.75	**1.75**	1.82	1.83	1.83	1.82	1.83	1.83	1.82	**1.83**
cwcc	1.75	1.77	1.76	1.75	1.76	1.76	1.76	**1.76**	1.83	1.85	1.84	1.83	1.84	1.85	1.83	**1.84**
O-cwcw	1.88	1.88	1.87	1.87	1.88	1.88	1.87	**1.88**	1.99	2.01	1.99	1.99	1.99	2.00	1.99	**1.99**
O-cccc[a]	*1.77*	*1.75*	*1.78*	*1.78*	*1.75*	*1.77*	*1.78*	***1.77***	*1.86*	*1.85*	*1.87*	*1.88*	*1.85*	*1.87*	*1.88*	***1.87***
***β*CD**	**PM3CARB-1**								**PM3-D***							
	glu1	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**	**glu1**	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**

cccw	1.86	1.86	1.85	1.85	1.86	1.86	1.85	**1.86**	1.83	1.82	1.83	1.83	1.82	1.84	1.85	**1.83**
cccc	1.86	1.86	1.86	1.86	1.86	1.86	1.86	**1.86**	1.82	1.82	1.84	1.83	1.82	1.84	1.83	**1.83**
cwcw	1.85	1.85	1.85	1.85	1.85	1.85	1.85	**1.85**	1.82	1.82	1.82	1.82	1.82	1.82	1.82	**1.82**
cwcc	1.85	1.85	1.85	1.85	1.85	1.85	1.85	**1.85**	1.83	1.83	1.83	1.83	1.83	1.83	1.83	**1.83**
O-cwcw	1.93	1.93	1.93	1.93	1.93	1.93	1.93	**1.93**	1.86	1.86	1.86	1.86	1.86	1.86	1.86	**1.86**
O-cccc	2.57	2.55	2.57	2.57	2.55	2.56	2.57	**2.56**	3.39	3.39	3.39	3.39	3.39	3.39	3.39	**3.39**
***β*CD**	**PM3**								**AM1**							
	glu1	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**	**glu1**	**glu2**	**glu3**	**glu4**	**glu5**	**glu6**	**glu7**	**avr**
cccw	1.83	1.85	1.86	1.85	1.82	1.84	1.85	**1.84**	2.15	2.15	2.15	2.15	2.15	2.15	2.14	**2.15**
cccc	1.82	1.82	1.84	1.83	1.82	1.85	1.83	**1.83**	2.16	2.16	2.16	2.16	2.17	2.16	2.15	**2.16**
cwcw	1.85	1.84	1.83	1.85	1.84	1.82	1.83	**1.84**	2.14	2.14	2.15	2.14	2.14	2.15	2.15	**2.14**
cwcc	1.83	1.83	1.83	1.83	1.83	1.83	1.83	**1.83**	2.15	2.16	2.16	2.15	2.15	2.16	2.16	**2.16**
O-cwcw	1.86	1.86	1.86	1.86	1.86	1.86	1.86	**1.86**	3.17	3.65	3.22	3.28	3.47	3.38	3.36	**3.36**
O-cccc[a]	*3.40*	*3.40*	*3.42*	*3.44*	*3.41*	*3.46*	*3.43*	***3.42***	*3.82*	*2.16*	*2.17*	*2.22*	*3.64*	*3.80*	*3.60*	***3.06***

[a]Collapsed open structure labelled in *italics*

Table S4 The relative energy (in kcal/mol) between cc/gGg⁻ and cw/tGg⁻ conformers, E_{cc-cw}.

Method	E_{cc-cw}	Method	E_{cc-cw}
HM-IE est. of CCSD(T)/cc-pVQZ[a]	0.35	**DFTB3**	0.59
MP2/def2-TZVPP	0.71	**SCC-DFTB**	0.42
MP2/aug-cc-pVTZ	0.73	**PM7**	−0.93
MP2/cc-pVDZ[b]	0.30	**PM6-DH2**	−1.30
M06-2X/def2-TZVPP	0.32	**PM6-D3**	−1.27
ωB97X-D/def2-TZVPP	0.17	**PM6**	−1.07
		PM3CARB-1	1.10
		PM3-D*	−1.39
		PM3	−1.39
		AM1	−0.88

[a]Ref. 45 [b]Ref. 17

Table S5 1,2-ethanediols geometries optimised at ab initio, DFT and semiempirical QM levels of theory[a]

diols	MP2/def2-TZVPP			MP2/aug-cc-pVTZ			M06-2X/def2-TZVPP			ωB97X-D/def2-TZVPP		
	φ_1	ψ	φ_2	φ_1	ψ	φ_2	φ_1	ψ	φ_2	φ_1	ψ	φ_2
cc/gGg$^-$	73	57	-43	74	57	-44	73	57	-43	72	58	-43
cw/tGg$^-$	-168	61	-50	-167	62	-51	-168	61	-51	-167	62	-52
diols	**DFTB3**			**SCC-DFTB**			**PM7**			**PM6-DH2**		
	φ_1	ψ	φ_2	φ_1	ψ	φ_2	φ_1	ψ	φ_2	φ_1	ψ	φ_2
cc/gGg$^-$	65	49	-25	61	54	-31	67	65	-42	73	52	-35
cw/tGg$^-$	-178	51	-39	-177	58	-45	-176	80	-58	-173	89	-62
diols	**PM6-D3**			**PM6**			**PM3CARB-1**			**PM3D***		
	φ_1	ψ	φ_2	φ_1	ψ	φ_2	φ_1	ψ	φ_2	φ_1	ψ	φ_2
cc/gGg$^-$	69	63	-43	68	76	-52	80	65	-49	64	70	-52
cw/tGg$^-$	-173	84	-61	-175	94	-66	-179	66	-63	-175	75	-61
diols	**PM3**			**AM1**								
	φ_1	ψ	φ_2	φ_1	ψ	φ_2						
cc/gGg$^-$	64	70	-51	66	60	-44						
cw/tGg$^-$	-174	75	-62	-175	64	-56						

[a]1,2-ethanediol structure shown in Figure 2; Dihedral angles in degrees: φ_1 ($H_bO_bC_bC_a$) ψ ($O_aC_aC_bO_b$) φ_2 ($H_aO_aC_aC_b$)

Table S6 Average distance between O atoms of the C2C3 rim of βCD and the graphene basal plane of βCD/$C_{96}H_{24}$ complexes (in Å) for DFT and semiempirical QM methods. Hydrogen bond network is underlined for the C2C3 rim.

Conformer	M06-2X/def2-SVP	DFTB3	PM7	PM6-DH2
cccw	2.96	3.05	2.92	3.10
cccc	2.98	3.04	2.85	3.07

Table S7 Interaction energies (IE) of βCD/$C_{1006}H_{88}$ complexes per glucosyl residue, calculated via PM6-DH2, PM7 and DFTB3 methods at C2C3 and C6 rims with respect to global energy minimum cccw conformer. Collapsed open structures labelled in italics. Energies in kcal/mol.

Conformer	**C2C3 adsorbed rim**			**C6 adsorbed rim**		
	DFTB3	**PM7**	**PM6-DH2**	**DFTB3**	**PM7**	**PM6-DH2**
cccw	-7.9	-8.9	-4.4	-4.9	-7.5	-3.5
cccc	-7.4	-10.0	-6.7	-5.1	-8.7	-5.7
cwcw	-7.2	-8.6	-4.3	-3.8	-7.2	-3.7
cwcc	-6.4	-9.9	-6.4	-4.1	-8.4	-5.5
O-cwcw	-5.1	-5.6	0.6	-4.2	-4.0	1.5
O-cccc	-3.4	*-9.0*	*-7.8*	-1.6	*-7.7*	*-5.6*

Table S8 Interaction energies (IE) of βCD/$C_{1006}H_{88}$ complexes per glucosyl residue, corrected for understabilisation of cccw conformer, calculated via PM6-DH2, PM7 and DFTB3 methods at C2C3 and C6 rims with respect to global energy minimum cccw conformer. Collapsed open structures labelled in italics. Energies in kcal/mol.

Conformer	**C2C3 adsorbed rim**			**C6 adsorbed rim**		
	DFTB3	**PM7**	**PM6-DH2**	**DFTB3**	**PM7**	**PM6-DH2**
cccw	-7.9	-8.9	-4.4	-0.1	-7.5	-3.5
cccc	-8.1	-8.7	-4.7	-0.2	-7.4	-3.7
cwcw	-7.8	-8.7	-4.3	-0.2	-7.3	-3.8
cwcc	-5.3	-8.6	-4.4	0.1	-7.1	-3.5
O-cwcw	-4.9	-7.4	-2.1	-0.1	-5.7	-1.2
O-cccc	-4.7	*-7.7*	*-5.8*	-0.2	*-6.4*	*-3.6*