Supplementary Information

Prism[*n*]arene-alkyl dibromide (*n* = 5, 6) synergy: Molecular affinity in the solid state

Mickey Vinodh, Nour O. Abdeljaber and Talal F. Al-Azemi*

Chemistry Department, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait.

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Table S1. Summary on the nature and various crystallographic parameters of **[PS-5 ⊃ DBH]**, [**[PS-5 ⊃ DBO], [PS-6 ⊃ DBH]**& **[PS-6⊃ DBO]**obtained after crystallization.

Crystal sample	**[PS-5 ⊃ DBH]**	**[PS-5 ⊃ DBO]**	**[PS-6⊃ DBH]**	**[PS-6⊃ DBO]**
Chemical formula	$C_{71}H_{72}Br_2O_{10}$	$C_{73}H_{76}Br_2O_{10}$	$C_{102}H_{120}Br_4O_{12}$	$C_{108}H_{128}Br_4O_{12}$
M_r	1245.10	1273.15	1857.61	1913.72
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, *Cc*	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*
Temperature (K)	296	296	296	296
a, *b*, *c* (Å)	11.1392 (5), 25.2833 (11), 22.6009 (12)	11.3658 (3), 25.1078 (7), 22.8023 (6)	38.7491 (9), 10.4816 (2), 23.9295 (5)	39.404 (2), 10.6754 (7), 24.3659 (14)
α, β, γ (°)	103.461 (2)	104.364 (1)	107.054 (1)	107.392 (4)
V (Å^3)	6190.4 (5)	6303.7 (3)	9291.7 (3)	9781.0 (10)
Z	4	4	4	4
Radiation type	Cu *K*α	Cu *K*α	Cu *K*α	Cu *K*α
μ (mm^{-1})	2.14	2.11	2.59	2.47
Crystal size (mm)	0.18 × 0.11 × 0.07	0.21 × 0.18 × 0.14	0.21 × 0.12 × 0.05	0.21 × 0.11 × 0.07
Diffractometer	Bruker *APEX*-II CCD Multi-scan	Bruker *APEX*-II CCD Multi-scan	Bruker *APEX*-II CCD Multi-scan	Bruker *APEX*-II CCD Multi-scan
Absorption correction	*SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction	*SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction	*SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction	*SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.69, 0.86	0.67, 0.76	0.50, 0.88	0.75, 0.91
No. of measured, independent & observed [$I > 2\sigma(I)$] reflections	45392, 5395, 4013	37239, 10363, 7259	63214, 8140, 6467	37950, 8578, 4850
R_{int}	0.063	0.044	0.059	0.068
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595	0.596	0.596	0.596
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.061, 0.185, 1.06	0.103, 0.318, 1.27	0.049, 0.144, 1.02	0.075, 0.257, 1.03
No. of reflections	5395	10363	8140	8578
No. of parameters	419	795	538	635
No. of restraints	95	132	16	246
H-atom treatment	Mixed	Constrained	Constrained	Constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.48	1.24, −0.70	0.57, −0.58	0.50, −0.36

Computer programs: *SHELXL2019*/3.

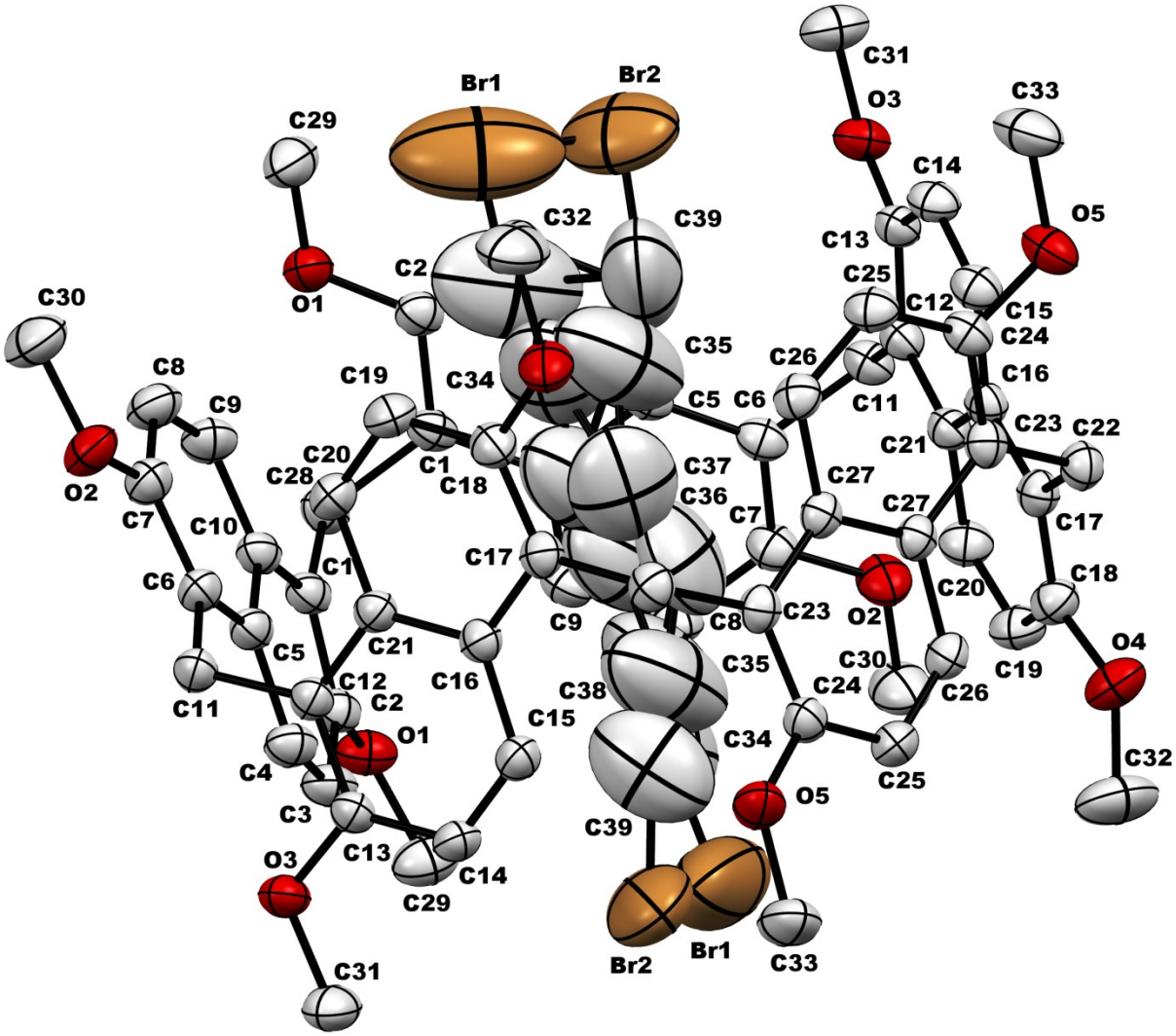

Figure S1. Thermal ellipsoid representation (30% probability) of **[PS-5 ⊃ DBH]**. (Hydrogen atoms are hidden for clarity)

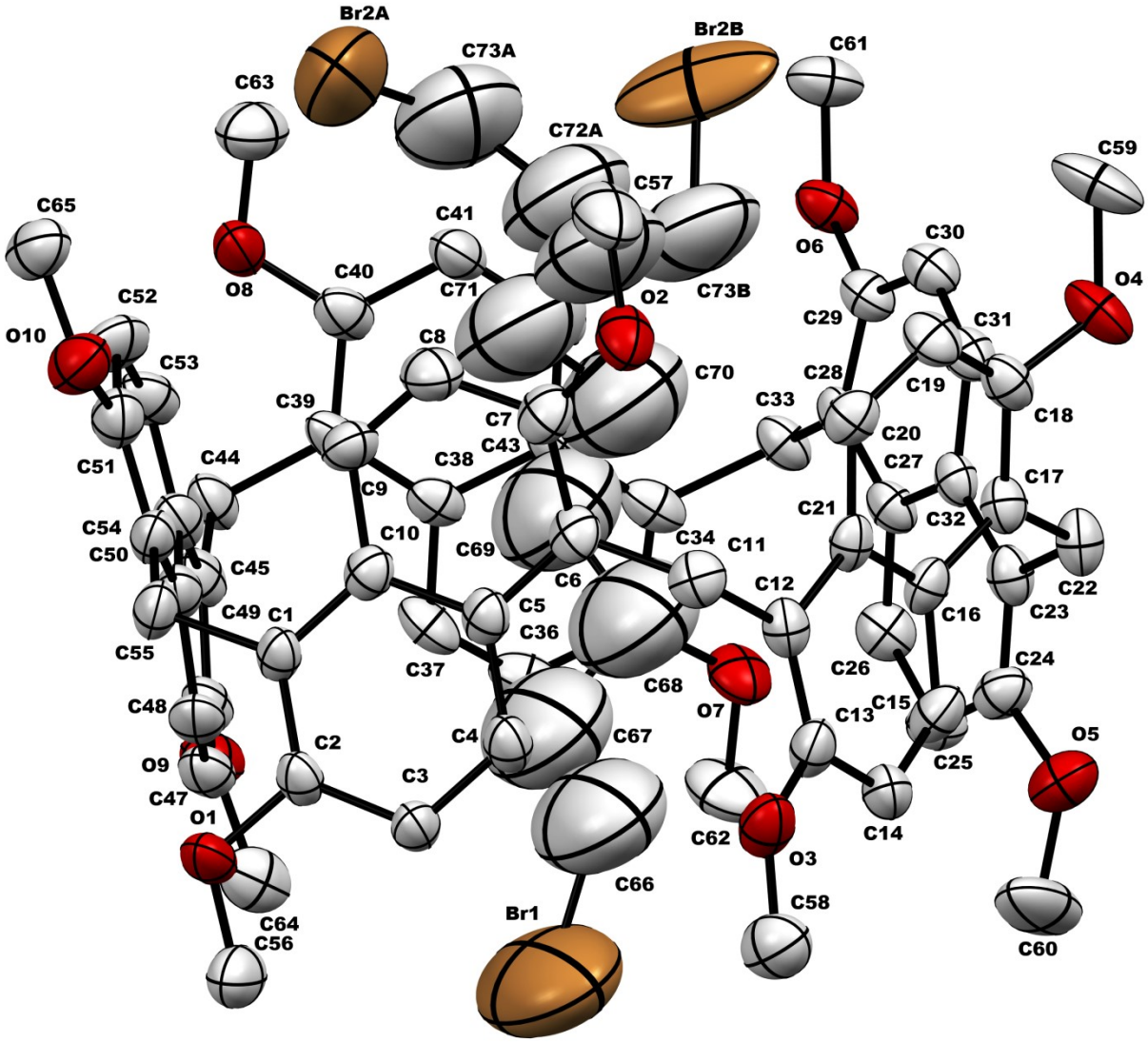

Figure S2. Crystal structure (thermal ellipsoid representation; 30% probability) of [**PS-5** ⊃ **DBO**]. (Hydrogen atoms are hidden for clarity)

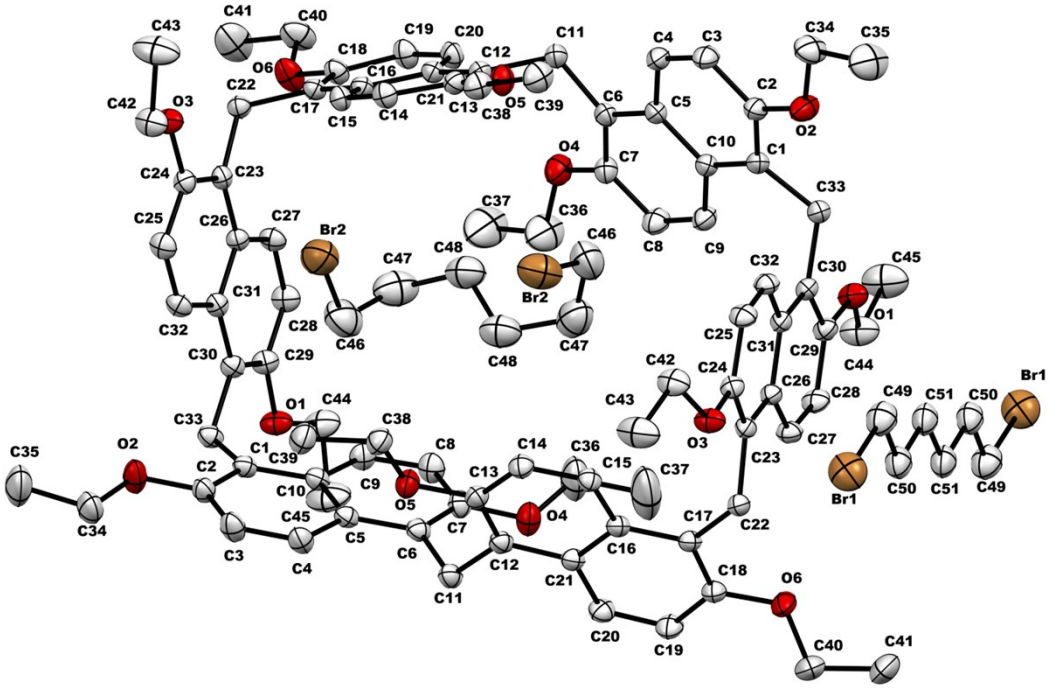

Figure S3. Thermal ellipsoid representation (30% probability) of **[PS-6 ⊃ DBH].** (Hydrogen atoms are hidden for clarity).

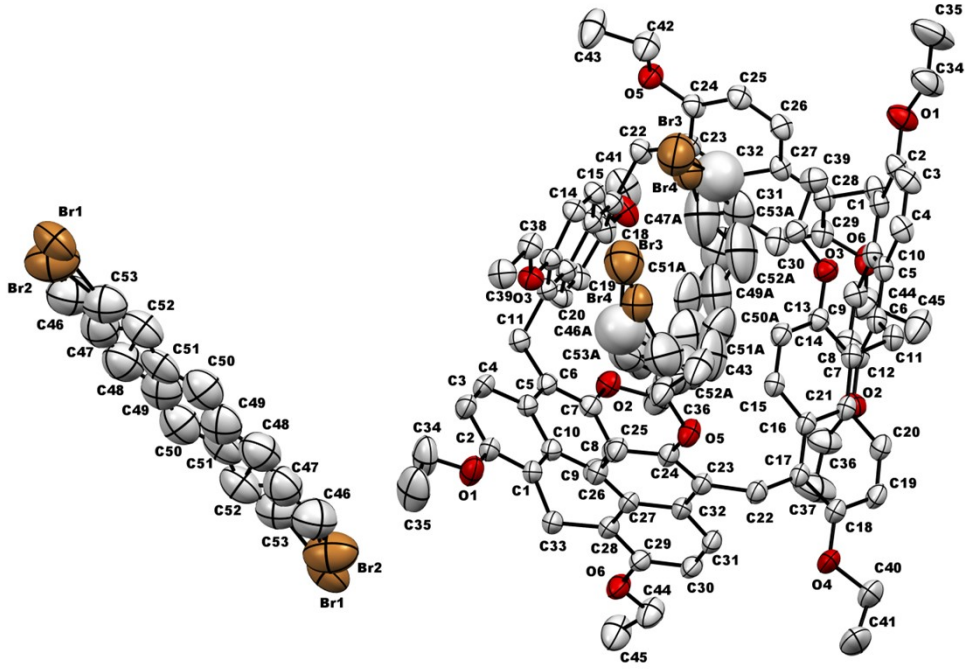

Figure S4. Crystal structure (thermal ellipsoid representation; 30% probability) of **[PS-6 ⊃ DBO]**. (Hydrogen atoms are hidden for clarity).

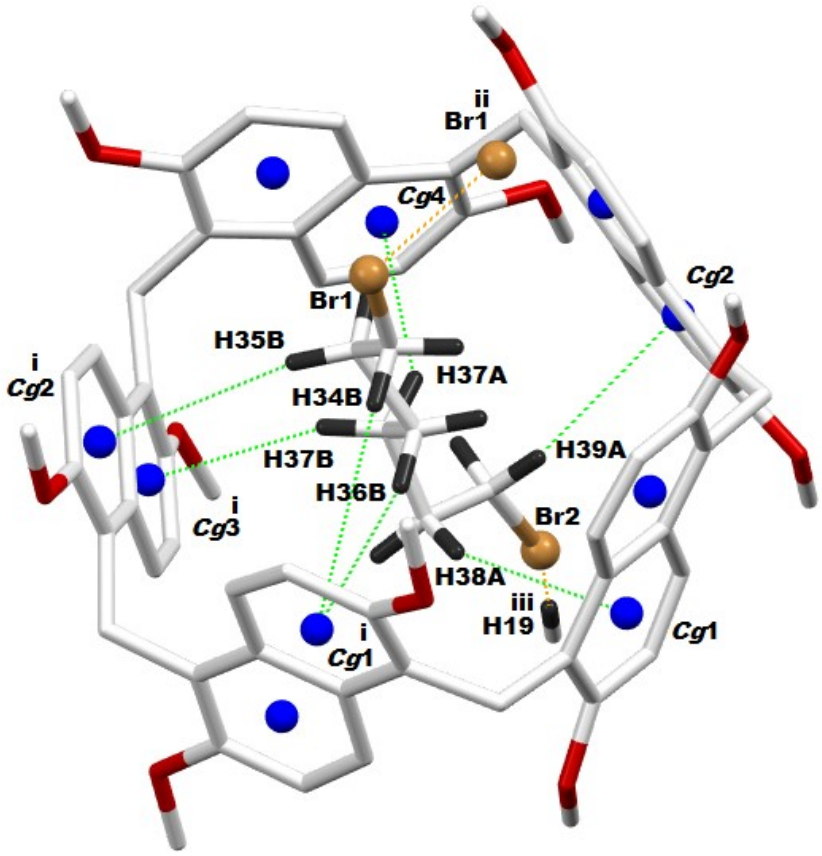

Figure S5. Possible noncovalent interactions in the crystal of [**PS-5** ⊃ **DBH**]. *Cg*1 – *Cg*4 are the centroid of the prism[5]arene phenyl rings constitute C1-5,C10; C12-16,C21; C16-C21 and C23-C27 respectively. Symmetry code: (i) 1-x, y, 1/2-z (ii) -x, y, 1/2-z and (iii) 1-x, y, z.

Table S2. Non-bonding interactions between prism[5]arene (**PS-5**) host and 1,6-dibromohexane (**DBH**) guest in the [**PS-5** ⊃ **DBH**] crystals (Å, °)

A-B···C	A-B	B···C	A···C	A-B···C
C34^{ii}-Br1^{ii}…Br1	1.63(2)	2.904(9)	4.08(3)	126.2(9)
C34-H34B… *Cg*1^{i}	0.97	3.493	4.405	157.65
C35-H35B…*Cg*2^{i}	0.97	3.366	4.286	159.16
C36-H36B…*Cg*1^{i}	0.97	3.198	4.134	162.26
C37-H37A…*Cg*4	0.97	3.375	4.210	145.47
C37-H37B…*Cg*3^{i}	0.97	3.071	3.958	152.49
C38-H38A…*Cg*1	0.97	3.411	4.325	157.83
C39-H39A…*Cg*2	0.97	3.086	4.012	160.17
C19^{iii}-H19^{iii}…Br2	0.93(3)	3.05(3)	3.978(4)	171(3)

*Cg*1 – *Cg*4 are the centroid of the prism[5]arene phenyl rings constitute C1-5,C10; C12-16,C21; C16-C21 and C23-C27 respectively. Symmetry code: (i) 1-x, y, 1/2-z (ii) -x, y, 1/2-z and (iii) 1-x, y, z.

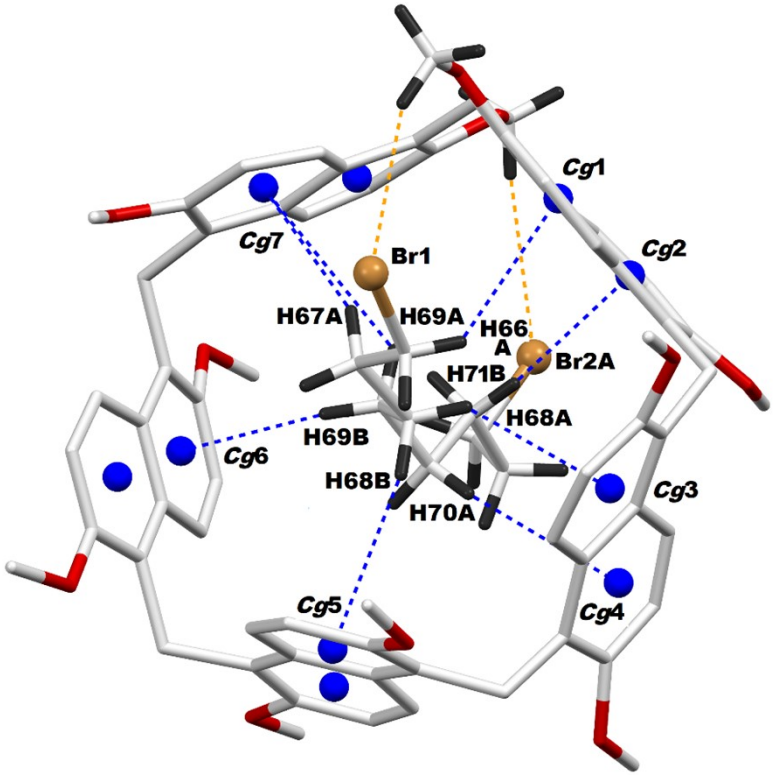

Figure S6. Possible noncovalent interactions in the crystal of [**PS-5** ⊃ **DBO**]. *Cg*1 – *Cg*7 are the centroids of the prism[5]arene phenyl rings constitute C1-5,C10; C5-C10; C12-16,C21; C16-C21; C23-C27, C32; C38-C43 and C45-C59,C54 respectively.

Table S3. Non-bonding interactions between prism[5]arene (**PS-5**) host and 1,8-dibromooctane (**DBO**) guest in the [**PS-5** ⊃ **DBO**] crystals (Å, °)

A-B···C	**A-B**	**B···C**	**A···C**	**A-B···C**
C56-H56B…Br1	0.96	3.078	3.96(2)	154.8
C66-H66A… *Cg*1	0.97	2.998	3.876	151.59
C67-H67A… *Cg*7	0.96	3.207	4.055	147.68
C68-H68A…*Cg*3	0.97	3.324	4.191	149.54
C68-H68B…*Cg*5	0.97	3.041	3.987	165.68
C69-H69A…*Cg*7	0.97	3.509	4.283	138.13
C69-H69B…*Cg*6	0.97	3.062	3.922	148.84
C70-H70A…*Cg*4	0.97	3.340	4.295	168.35
C71-H71A…*Cg*2	0.96	3.034	4.001	174.60
C65-H65B…Br2A	0.96	3.00	3.94(2)	163.8

*Cg*1 – *Cg*7 are the centroids of the prism[5]arene phenyl rings constitute C1-5,C10; C5-C10; C12-16,C21; C16-C21; C23-C27, C32; C38-C43 and C45-C59,C54 respectively.

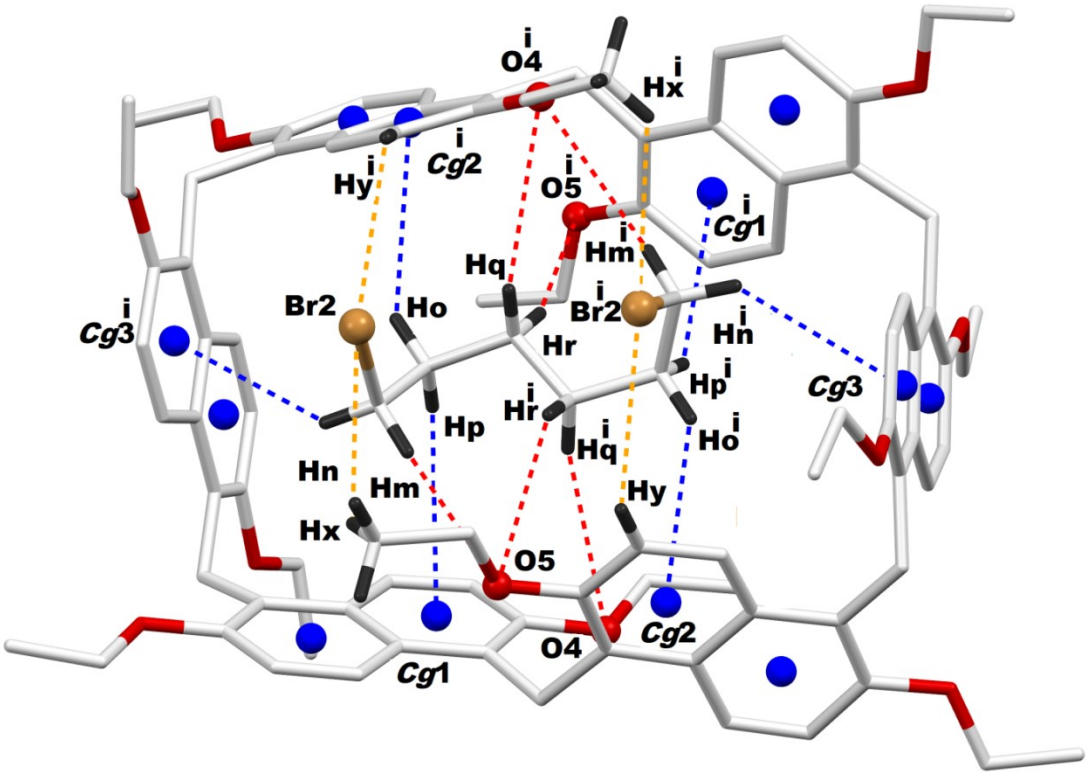

Figure S7. Possible noncovalent interactions in the crystal of [**PS-6** ⊃ **DBH**]. *Cg*1 - *Cg*3 are the centroids of the prismarene phenyl rings constitute C5-C10; C12-16, C21 and C23-C26, C31,C32 respectively and symmetry code (^{i}) is 1-x, y, 1/2-z; H_m = H46A; H_n = H46B; H_o = H47A; H_p = H47B; H_q = H48A; H_r = H48B; H_x = H39A & H_y = H14.

Table S4. Non-bonding interactions between prism[6]arene (**PS-6**) host and 1,6-dibromohexane (**DBH**) guest in the [**PS-6** ⊃ **DBH**] crystals (Å, °)

A-B···C	**A-B**	**B···C**	**A…C**	**A-B···C**
C14-H14…Br2	0.93	3.3081	3.835(3)	118.1
C39-H39A… Br2	0.96	3.2881	3.842(4)	118.6
C46-H46A…O5	0.97	3.106	4.058(5)	167.1
C46-H46B…*Cg*3	0.97	3.221	3.979	136.24
C47-H47A…*Cg*2	0.97	3.229	4.042	142.34
C47-H47B…*Cg*1	0.97	3.378	4.098	132.71
C48-H48A…O4	0.97	3.330	4.272(6)	164.4
C48-H48B…O5	0.97	3.161	3.895(6)	133.7

*Cg*1 - *Cg*3 are the centroids of the prismarene phenyl rings constitute C5-C10; C12-16, C21; C23-C26, C31, C32 respectively.

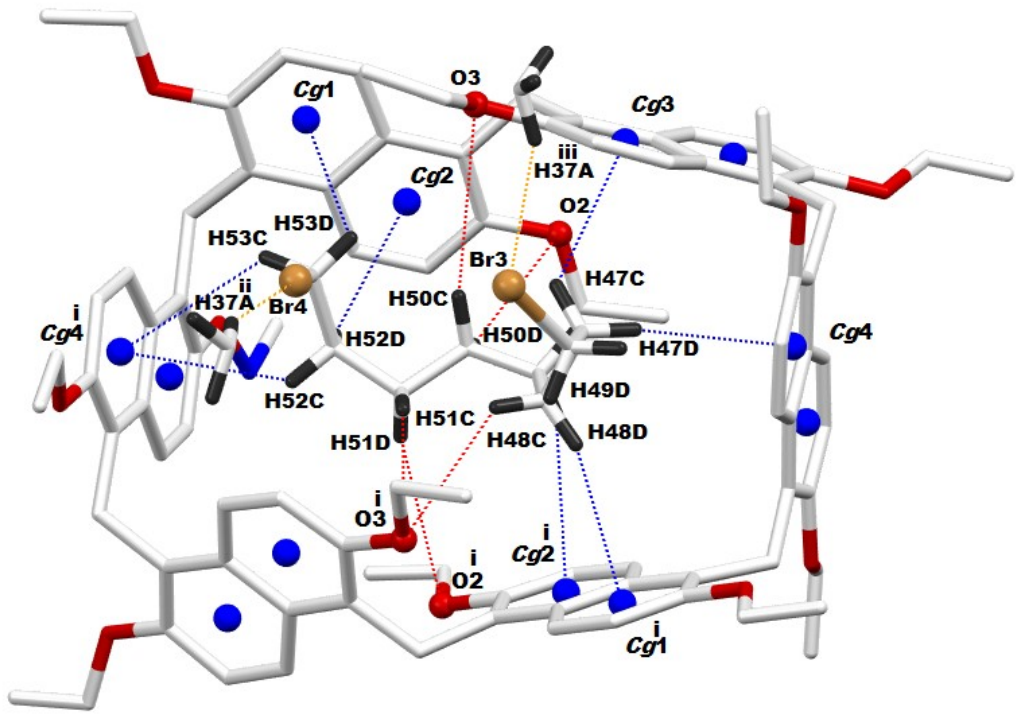

Figure S8. Possible noncovalent interactions in the crystal of [**PS-6** ⊃ **DBO**]. *Cg*1 – *Cg*4 are the centroid of the prism[5]arene phenyl rings constitute C1-5,C10; C5-C10; C12-16,C21; C23-C27,C32 respectively. Symmetry code: (i) 1-x, y, 1.5-z; (ii) x, -1+y, z; (iii) 1-x, -1+y, 1.5-z.

Table S5. Non-bonding interactions between prism[6]arene (**PS-6**) host and 1,8-dibromooctane (**DBO**) guest in the [**PS-6** ⊃ **DBO**] crystals (Å, °)

A-B…C	**A-B**	**B…C**	**A…C**	**A-B…C**
C37^{ii}-H37A^{ii}…Br3	0.96	2.819	3.71(1)	155.1
C47A-H47C… *Cg*3	0.97	3.353	4.034	128.81
C47A-H47D… *Cg*4	0.97	3.842	3.749	156.22
C48A-H48C… O3^{i}	0.97	3.095	3.87(5)	138
C48A-H48D… *Cg*1^{i}	0.97	3.087	4.001	158.26
C49A-H49D… *Cg*2^{i}	0.97	3.248	3.914	127.24
C50A-H50C… O3	0.97	3.439	4.36(2)	160
C50A-H50D … O2	0.97	3.284	4.05(2)	137
C51A-H51C… O3^{i}	0.97	3.309	4.20(2)	154
C51A-H51D … O2^{i}	0.97	3,149	4.03(3)	151
C52A-H52C… *Cg*4^{i}	0.97	3.187	3.846	126.29
C52A-H52D… *Cg*2	0.97	3.345	4.110	137.37
C53A-H53C… *Cg*4^{i}	0.97	3.202	3.882	128.78
C53A-H53D… *Cg*1	0.97	3.482	3.960	112.70
C37^{iii}-H37A^{iii}…Br4	0.96	3.517	4.43(1)	160.1

*Cg*1 – *Cg*4 are the centroid of the prism[5]arene phenyl rings constitute C1-5,C10; C5-C10; C12-16,C21; C23-C27,C32 respectively Symmetry code: (i) 1-x, y, 1.5-z; (ii) x, -1+y, z; (iii) 1-x, -1+y, 1.5-z.

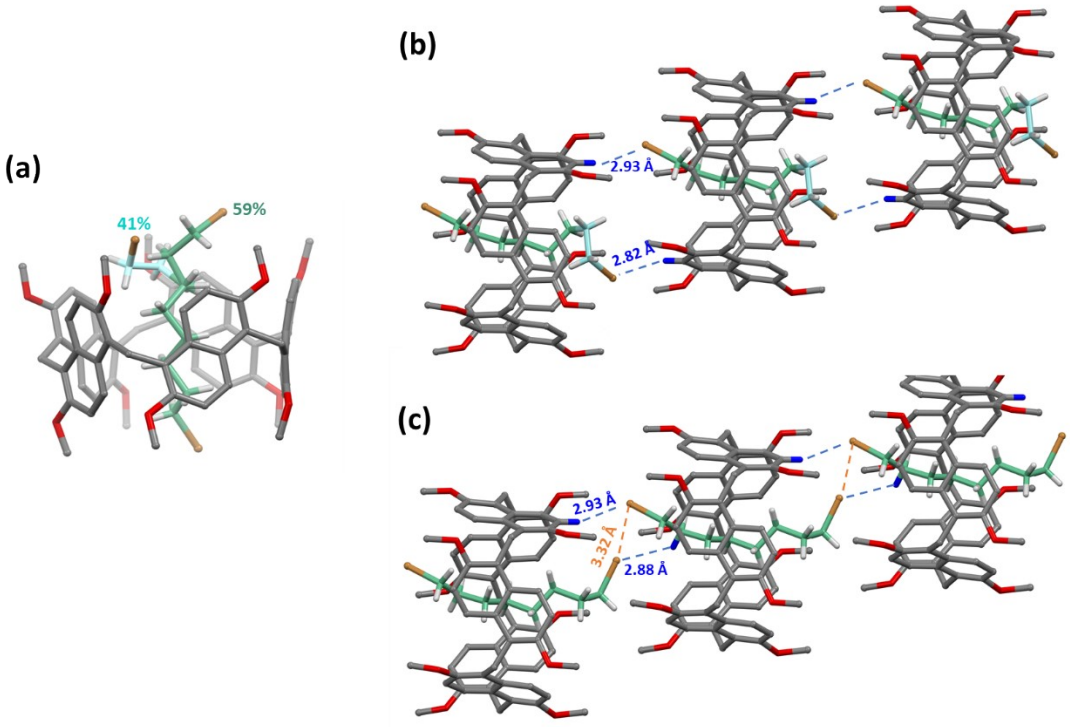

Figure S9. Crystal structures of the inclusion complexes based on prism[5]arene with 1,8-dibromooctane (**DBO**) (a), linear supramolecular polymer backbone driven by the minor occupancy guest conformations (b) and major occupancy guest conformations (c).

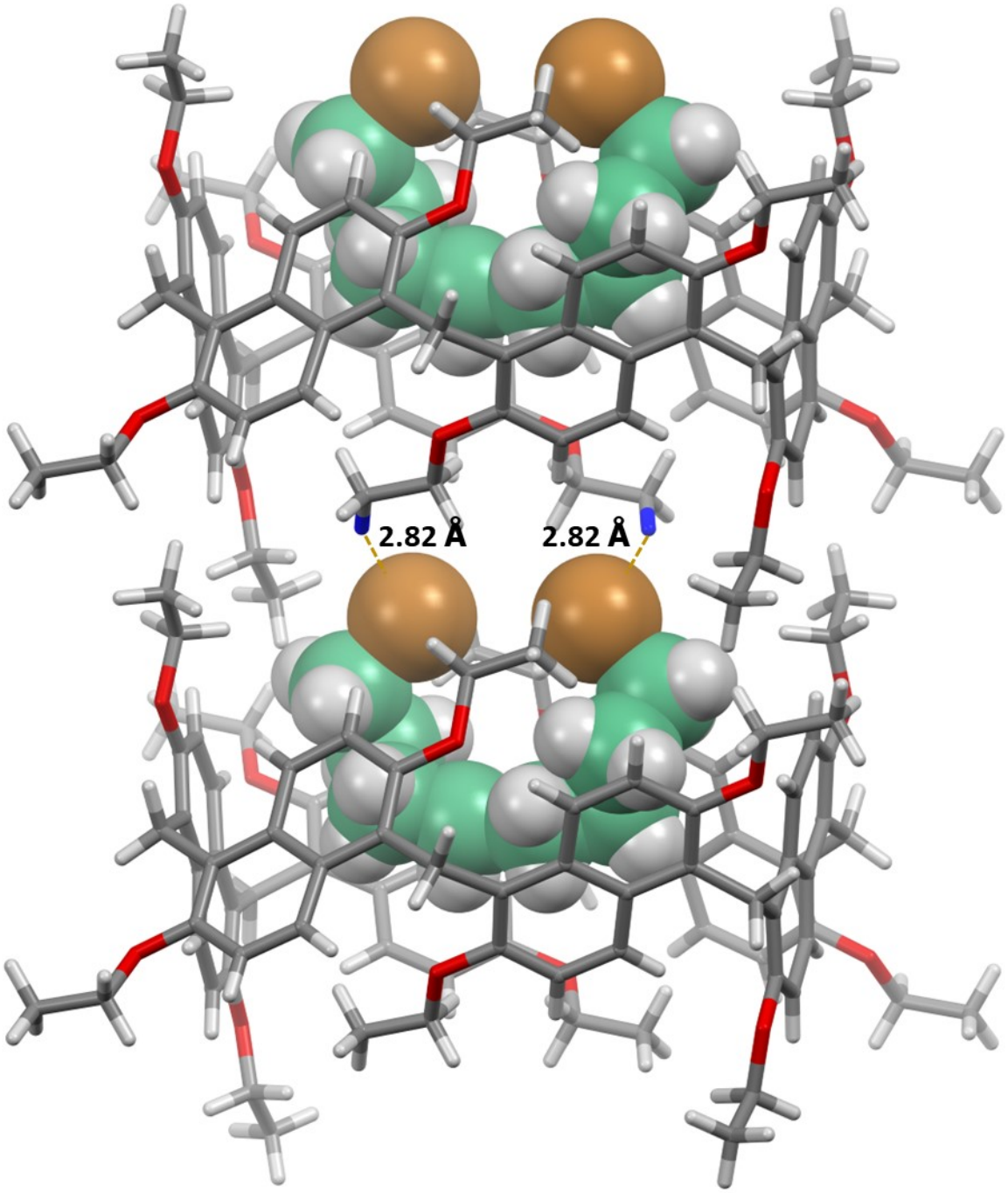

Figure S10. Intermolecular Br···H-C interactions in crystal structures of the inclusion complexes based on prism[5]arene with 1,8-dibromooctane (**PS-6 ⊃ DBO**).

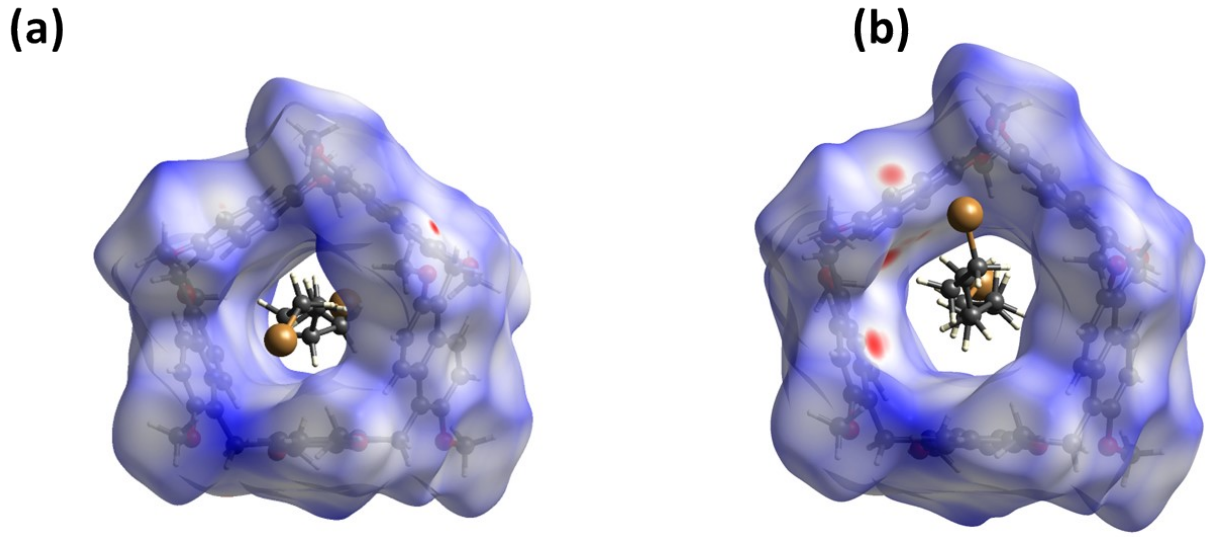

Figure S11. Hirshfeld surfaces (mapped with dnorm) illustrating the interaction modes inside the prism[5]arene cavity for [**PS-5 ⊃ DBH**] (**a**) and [**PS-5 ⊃ DBO**] (**b**).