Electronic Supplementary Material (ESI) for CrystEngComm.

Endo-/*Exo*- and halogen bond complexes of conformationally rigid C-ethyl-2-bromoresorcinarene and aromatic *N*-oxides

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Supporting Information

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I General Information

All the solvents used for syntheses and crystal growth are reagent grade, and are used as received. Pyridine *N*-oxide (**1**), 2-methylpyridine *N*-oxide (**2**), 3-methylpyridine *N*-oxide (**3**), 4-methylpyridine *N*-oxide (**4**), 4-methoxypyridine *N*-oxide (**5**), 2,4,6-trimethylpyridine *N*-oxide (**6**), 4-phenylpyridine *N*-oxide (**7**), isoquinoline *N*-oxide **(8**), quinoline *N*-oxide (**9**) and 4,4'-bipyridine *N,N*'-dioxide (**10**) were purchased from Sigma Aldrich. C-ethyl-2-Bromoresorcinarene (BrC2) and 1,3-(bispyridyl)propane N,N'-dioxide (**11**) were synthesized according to reported procedures.[1]

II Solid-state analyses

(a) X-ray experimental

Single-crystal X-ray data for **acetone**@BrC2, **1**@BrC2, **2**@BrC2, **3**@BrC2, **4**@BrC2, (acetone@BrC2)•**7**, (acetone@BrC2)•**8**, **9**@BrC2 and (acetone@BrC2)•**11**, were collected at either 120.0 K or 123.0 K on a dual source Rigaku SuperNova Oxford diffractometer equipped with an Atlas detector using a mirror-monochromated Cu-Kα (λ = 1.54184 Å) radiation. The data for (acetone@BrC2)•**5,** (acetone@BrC2)•**6** and (acetone@BrC2)•**10** were measured at either 120.0 K or 123.0 K using a Rigaku SuperNova single-source Oxford diffractometer with an Atlas EoS CCD detector using mirror-monochromated Mo-*K*α (λ = 0.71073 Å) radiation. The data collection and reduction for all complexes were performed using the program *CrysAlisPro*.[2] The gaussian face index absorption correction method[2] was used for all complexes, and the structures were solved with direct methods (*SHELXS*[3]) and refined by full-matrix least squares on F^2 using the *OLEX 2* software,[4] which utilizes the *SHELXL*-2013 module.[3] No attempt was made to locate the hydrogens for disordered solvent molecules; some hydrogen atoms involved in hydrogen bonds were introduced from difference Fourier maps. Constraints and restraints are used where appropriate for disordered models.

Table S1. X-Ray Experimental details for **acetone**@BrC2 to **3**@BrC2

Complex	**acetone**@BrC2	**1**@BrC2	**2**@BrC2	**3**@BrC2
CCDC No:	1551401	1551402	1551403	1551404
Empirical formula	$C_{41}H_{45}Br_4O_{10}$	$C_{49}H_{52}Br_4N_2O_{11}$	$C_{51}H_{56}Br_4N_2O_{11}$	$C_{51}H_{56}Br_4N_2O_{11}$
Formula weight	1017.41	1164.56	1192.61	1192.61
Temperature (K)	123.0	120.0	120.0	120.0
Crystal system	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	*Pmmn*	*P*-1	*P*-1	*P*-1
Unit cell dimensions: a (Å)	16.2181(9)	13.7077(4)	13.8485(6)	13.6699(3)
b (Å)	16.1822(8)	13.9155(4)	13.9210(4)	13.7198(4)
c (Å)	7.9215(4)	13.9398(4)	14.3337(4)	14.7020(5)
α (°)	90	90.621(2)	90.848(2)	114.673(3)
β (°)	90	116.716(3)	115.869(4)	90.898(2)
γ (°)	90	96.052(2)	90.012(3)	92.597(2)
Volume / $Å^3$	2078.96(19)	2356.84(13)	2486.07(17)	2501.22(13)
Z	2	2	2	2
Density (calculated) mg/m^3	1.625	1.641	1.593	1.584
Absorption Coefficient mm^{-1}	5.191	4.695	4.466	4.439
F(000)	1022	1176	1208	1208
Crystal size (mm^3)	0.16 x 0.04 x 0.02	0.20 x 0.11 x 0.05	0.11 x 0.09 x 0.05	0.20 x 0.11 x 0.47
θ range for data collection (°)	5.58 to 66.74	3.20 to 66.75	3.42 to 66.75	3.30 to 66.75
Reflections collected	9568	13651	16207	14656
[R(int)]	[0.0646]	[0.0256]	[0.0351]	[0.0297]
Reflections [I>2sigma(I)]	1706	7560	7754	7850
Data completeness (%)	99.54	99.04	99.13	99.04
Data/ restraints/ parameters	1981/6/153	8284/2/ 621	8742/8/641	8799/4/641
Goodness-of-fit on F^2	1.059	1.028	1.089	1.046
Final R_1 indices [I>2sigma(I)]	R_1 = 0.0408, wR_2 = 0.1006	R_1 = 0.0294, wR_2 =0.0733	R_1 = 0.0381, wR_2 = 0.0931	R_1 = 0.0289, wR_2 = 0.0705
Final R indices [all data]	R_1 = 0.0497, wR_2 = 0.1057	R_1 = 0.0327, wR_2 =0.0760	R_1 = 0.0438, wR_2 = 0.0966	R_1 = 0.0334, wR_2 = 0.0741
Largest diff. peak/hole ($e.Å^{-3}$)	0.657/ -0.669	1.379/ -0.739	0.802/ -0.568	0.427/ -0.439

Table S2. X-Ray Experimental details for **4**@BrC2 to (**acetone**@BrC2)•**7**

Complex	**4**@BrC2	(**acetone**@BrC2)•**5**	(**acetone**@BrC2)•**6**	(**acetone**@BrC2)•**7**
CCDC No:	1551405	1551406	1551407	1551408
Empirical formula	$C_{54}H_{57}Br_4N_3O_{11}$	$C_{57}H_{68}Br_4N_2O_{15}$	$C_{50}H61Br_4NO_{12}$	$C_{72}H_{69}Br_4N_3O_{12}$
Formula weight	1243.66	1340.77	1187.63	1487.94
Temperature (K)	120.0	120.0	120.0	123.0
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*$P2_1/n$*	*C2/c*	*P2/c*	*P2/n*
Unit cell dimensions: a (Å)	13.8438(4)	31.3059(19)	15.3678(8)	19.2354(5)
b (Å)	26.2609(6)	8.0079(5)	7.9991(3)	7.84234(14)
c (Å)	14.0294(3)	23.0375(17)	22.9088(11)	22.8722(6)
α (°)	90	90	90	90
β (°)	91.720(2)	96.653(7)	104.628(5)	114.269(3)
γ (°)	90	90	90	90
Volume / $Å^3$	5098.1(2)	5736.5(7)	2724.8(2)	3145.36(14)
Z	4	4	4	2
Density (calculated) mg/m^3	1.620	1.552	1.448	1.571
Absorption Coefficient mm^{-1}	4.390	2.875	3.011	3.681
F(000)	2520	2736	1208	1516
Crystal size (mm^3)	0.10 x 0.07 x 0.02	0.17 x 0.04 x 0.02	0.28 x 0.07 x 0.04	0.07 x 0.05 x 0.03
θ range for data collection (°)	3.57 to 66.74	2.80 to 25.25	3.14 to 25.25	3.90 to 66.74
Reflections collected [R(int)]	17258 [0.0306]	14479 [0.0650]	11117 [0.0290]	17556 [0.0611]
Reflections [I>2sigma(I)]	7747	3895	4052	4769
Data completeness (%)	98.66	99.76	98.67	99.87
Data/ restraints/ parameters	8948 /0/658	5192 /0/ 354	4906/7/345	5578 /41/456
Goodness-of-fit on F^2	1.137	1.146	1.044	1.020
Final R_1 indices [I>2sigma(I)]	R_1 = 0.0757, wR_2 = 0.2028	R_1 = 0.0818, wR_2 = 0.2002	R_1 = 0.0467, wR_2 = 0.1334	R_1 = 0.0451, wR_2 = 0.1081
Final R indices [all data]	R_1 = 0.0835, wR_2 = 0.2078	R_1 = 0.1101, wR_2 = 0.2131	R_1 = 0.0599, wR_2 = 0.1434	R_1 = 0.0539, wR_2 = 0.1147
Largest diff. peak/hole ($e.Å^{-3}$)	3.745 / -1.002	1.681 / -0.944	1.525/ -1.223	1.435 / -0.499

Table S3. X-Ray Experimental details for (**acetone**@BrC2)•**8** to (**acetone**@BrC2)•**11**

Complex	(**acetone**@BrC2)•**8**	**9**@BrC2	(**acetone**@BrC2)•**10**	(**acetone**@BrC2)•**11**
CCDC No:	1551409	1551410	1551411	1551412
Empirical formula	$C_{60}H_{62}Br_4N_2O_{12}$	$C_{57}H_{56}Br_4N_2O_{11}$	$C_{75}H_{78}Br_4N_6O_{17}$	$C_{56}H_{72}Br_4N_2O_{16}$
Formula weight	1322.75	1264.67	1655.07	1350.81
Temperature (K)	123.0	120.0	120.0	123.0
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*$P2_1/n$*	*C2/c*	*P2/n*
Unit cell dimensions: a (Å)	25.3967(6)	14.1188(3)	37.615(8)	14.85237(16)
b (Å)	7.78520(18)	26.2939(6)	7.8003(16)	7.94141(8)
c (Å)	27.8052(8)	14.3240(3)	27.830(6)	24.9573(2)
α (°)	90	90	90	90
β (°)	96.897(2)	91.644(2)	120.42(3)	91.3906(9)
γ (°)	90	90	90	90
Volume / $Å^3$	5457.8(2)	5315.4(2)	7042(3)	2942.81(5)
Z	4	4	4	2
Density (calculated) mg/m^3	1.610	1.580	1.561	1.524
Absorption Coefficient mm^{-1}	4.150	4.218	2.362	3.907
F(000)	2688	2560	3384	1384
Crystal size (mm^3)	0.10 x 0.04 x 0.02	0.23 x 0.07 x 0.07	0.17 x 0.08 x 0.05	0.19 x 0.13 x 0.11
θ range for data collection (°)	3.68 to 66.73	4.34 to 66.74	1.52to 25.25	2.98 to 66.74
Reflections collected [R(int)]	9166 [0.0324]	35634 [0.0534]	21198 [0.0303]	15504 [0.0289]
Reflections [I>2sigma(I)]	4424	7891	5827	4901
Data completeness (%)	98.71	99.63	99.88	99.81
Data/ restraints/ parameters	4865/19/378	9404/0/675	6382 /0/466	5219/0/436
Goodness-of-fit on F^2	1.125	1.173	1.053	1.028
Final R_1 indices [I>2sigma(I)]	R_1 = 0.0549, wR_2 = 0.1512	R_1 = 0.0873, wR_2 = 0.2170	R_1 = 0.0566, wR_2 = 0.1443	R_1 = 0.0269, wR_2 = 0.0664
Final R indices [all data]	R_1 = 0.0631, wR_2 = 0.1626	R_1 = 0.1002, wR_2 = 0.2249	R_1 = 0.0605, wR_2 = 0.1499	R_1 = 0.0288, wR_2 = 0.0679
Largest diff. peak/hole ($e.Å^{-3}$)	3.507 / -0.848	4.545 / -0.778	3.166/ -0.787	0.658/ -0.690

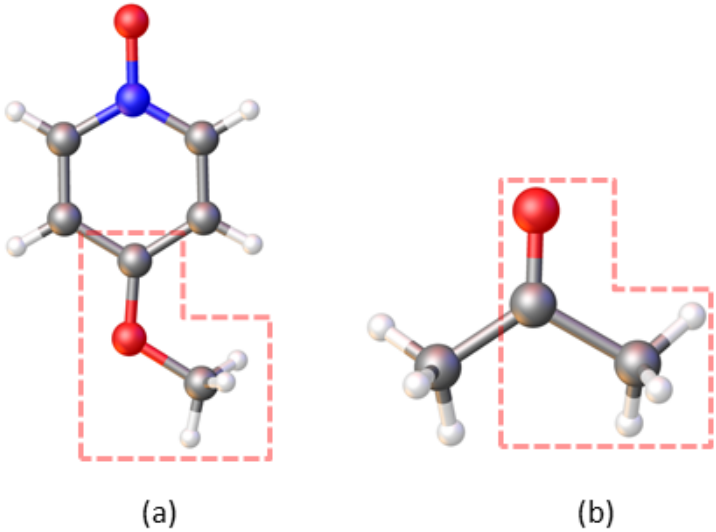

Fig. S1 Comparison of (a) guest **5**, and (b) acetone for *endo*-cavity complexation.

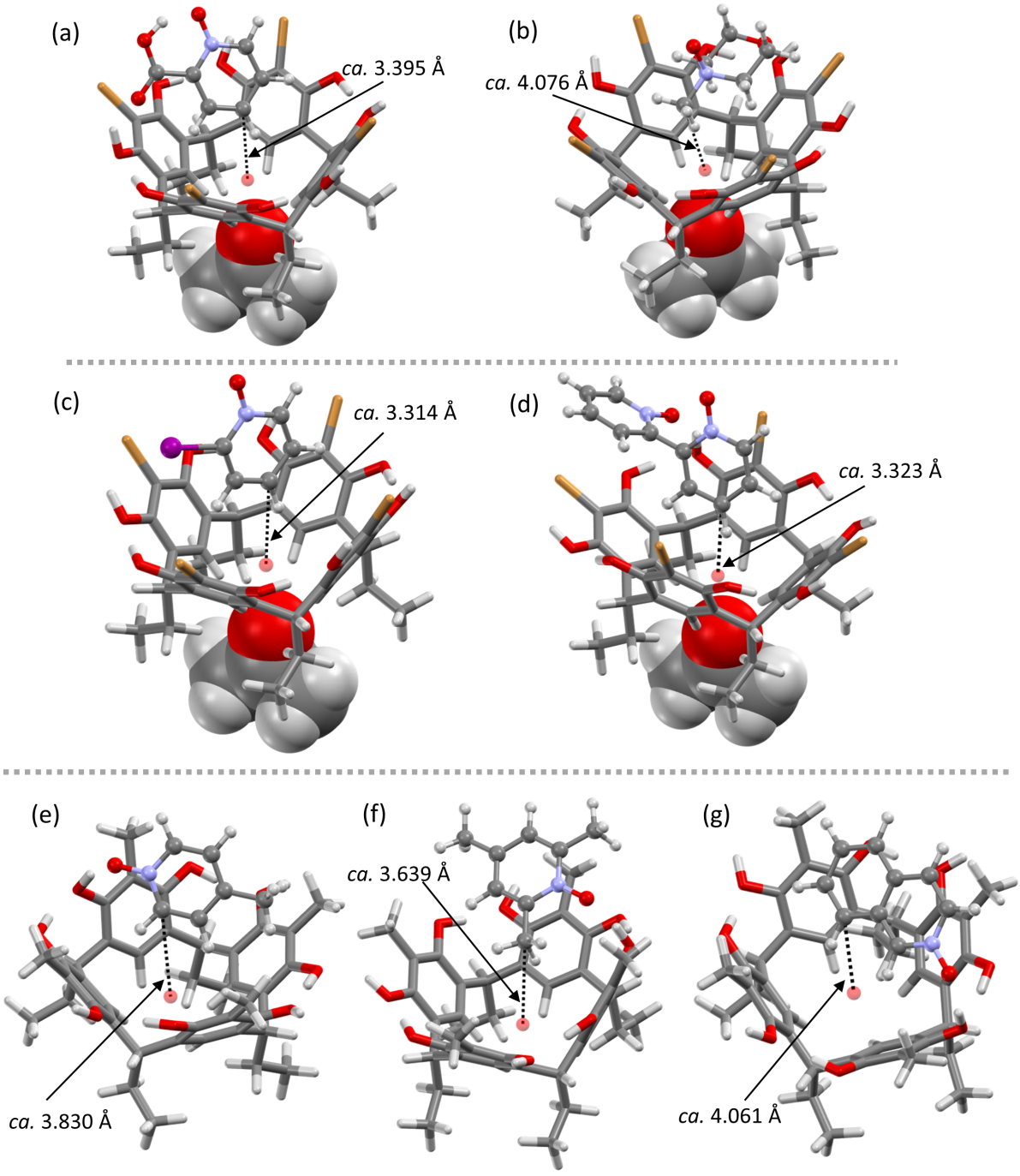

Fig. S2 Energy optimized structure to show the position of the guest inside the cavity for complexes (a) **12**@BrC2, (b) **13**@BrC2 (c) **14**@BrC2, (d) **15**@BrC, (e) **4**@MeC2, (f) **6**@MeC2 and (g) **8**@MeC2. The host is shown as a capped stick model, and the guest as a ball-stick model; lower rim acetones are represented using a CPK model. The position of the guest molecule is calculated from the centroid of the lower carbon atom-ring of the host.

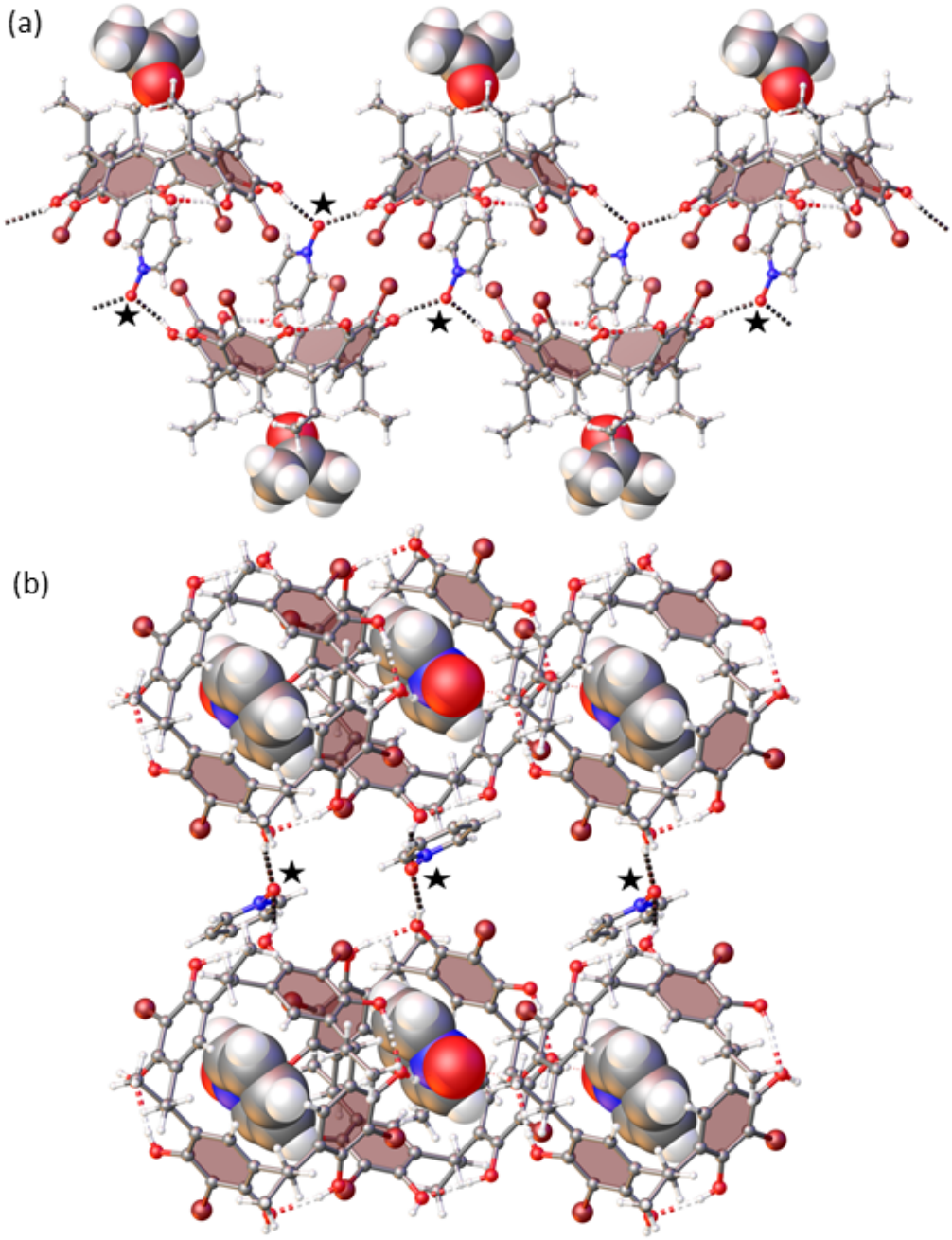

Fig. S3 (a) Section of the 3-D crystal packing to show *endo*-cavity guest **1** as a bidentate hydrogen acceptor for the host hydroxyl groups in **1**@BrC2; (b) Section of the 3-D crystal packing to show *exo*-cavity guest **1** as a bidentate hydrogen acceptor for the host hydroxyl groups in complex **1**@BrC2. The bidentate oxygen in guest molecules is marked with 'stars'.

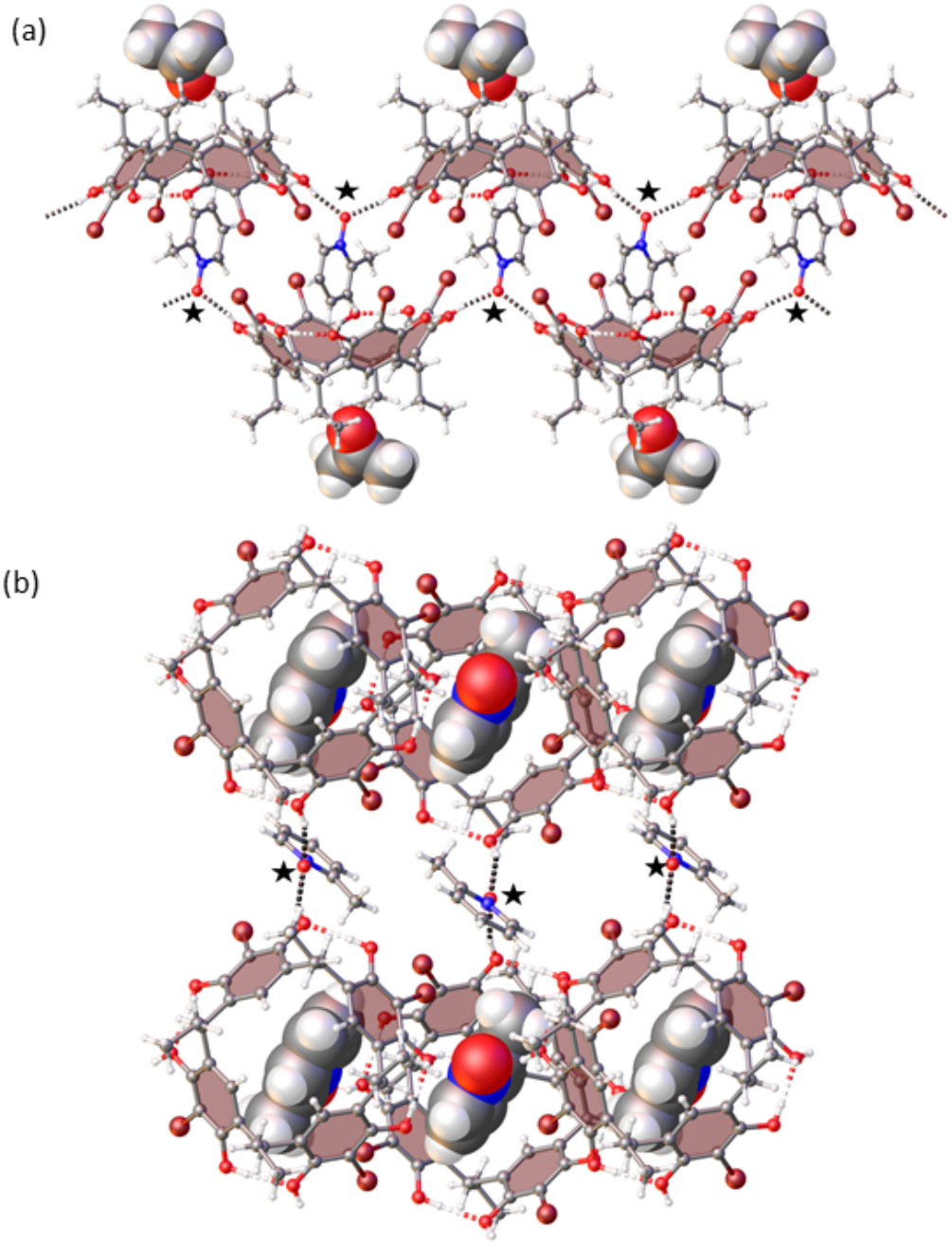

Fig. S4 (a) Section of the 3-D crystal packing to show *endo*-cavity guest **2** acting as a bidentate hydrogen acceptor for host hydroxyl groups in complex **2**@BrC2; (b) Section of the crystal packing to show *exo*-cavity guest **2** as a bidentate hydrogen acceptor for host hydroxyl groups in complex **2**@BrC2. The bidentate oxygen in guest molecules is marked with 'stars'.

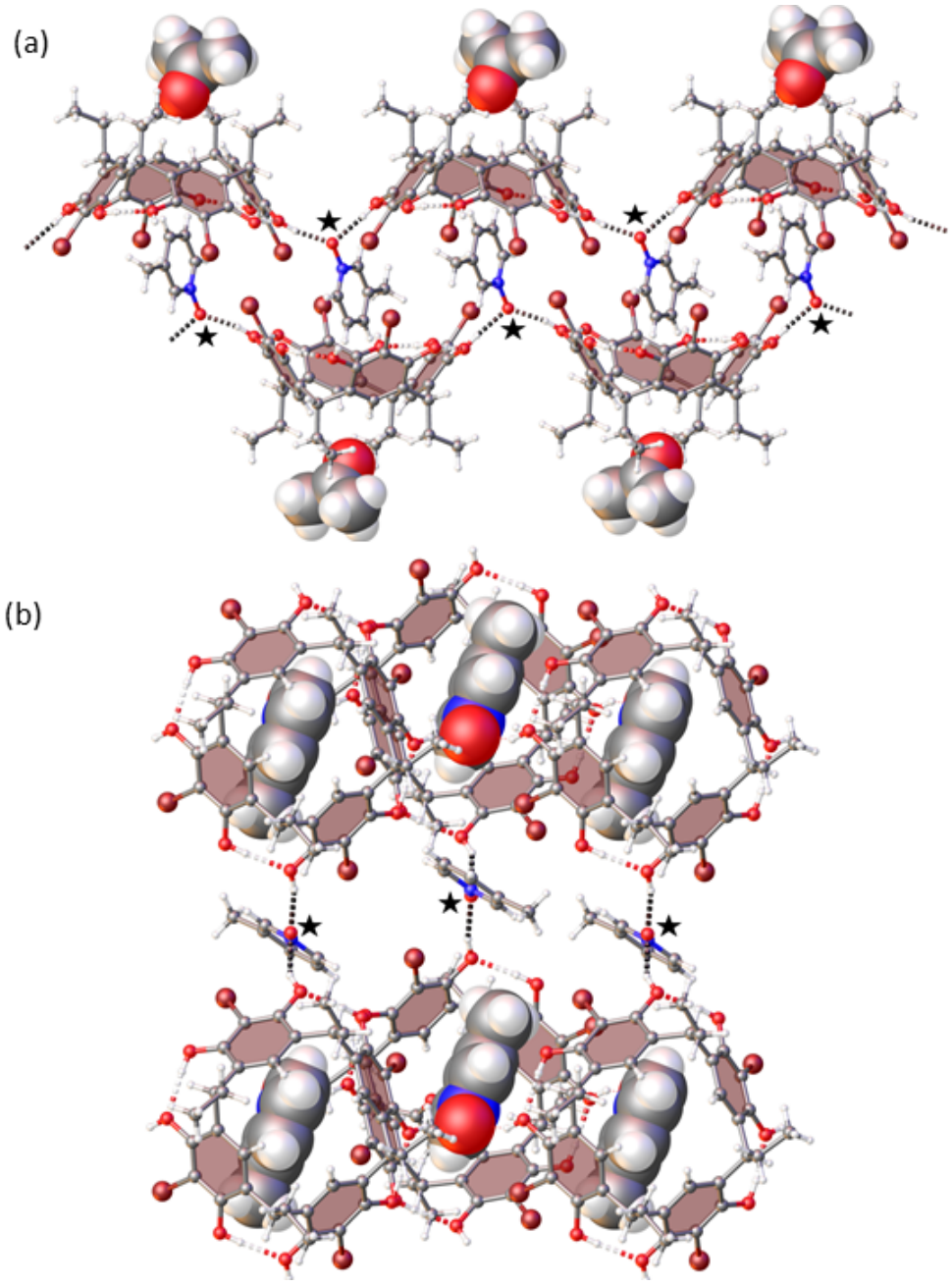

Fig. S5 (a) Section of the crystal packing to show in-cavity guest **3** acting as a bidentate hydrogen acceptor for two host hydroxyl groups in complex **3**@BrC2; (b) Section of the crystal packing to show out-of-cavity guest **3** acting as a bidentate hydrogen acceptor for two host hydroxyl groups in complex **3**@BrC2. The bidentate oxygens of guest molecules are marked with 'stars'.

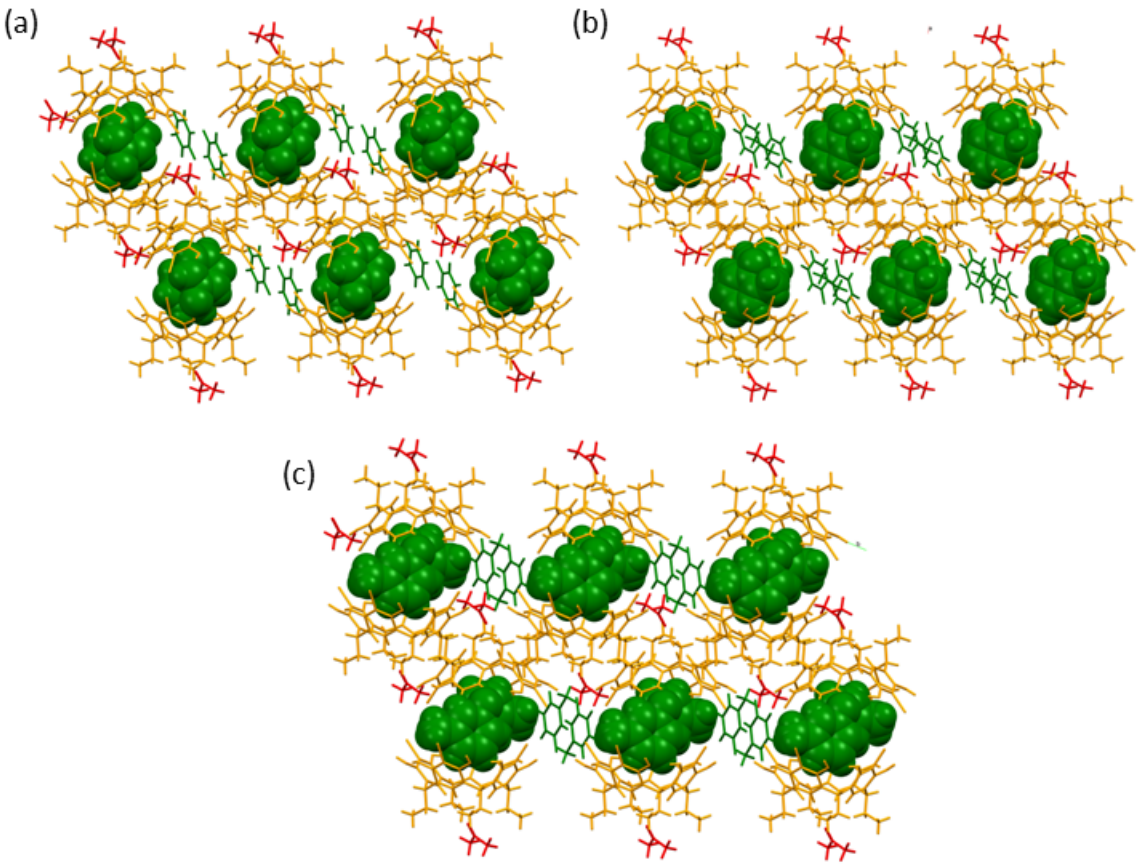

Fig. S6 Comparison of the 3-D crystal packing in complexes (a) **1**@BrC2 (b) **2**@BrC2 and (c) **3**@BrC2. Colour representation: gold - host, green - aromatic N-oxide and red - acetone molecules.

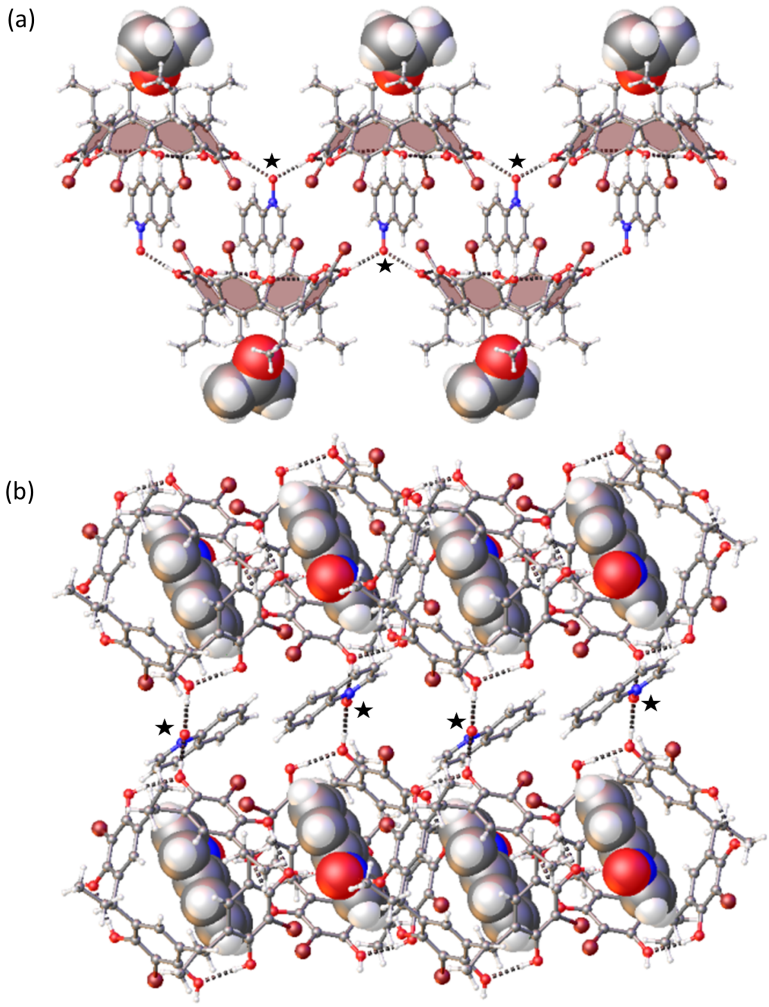

Fig. S7 (a) Section of the 3-D crystal packing to show *endo*-cavity guest **9** as a bidentate hydrogen acceptor for the host hydroxyl groups in **9**@BrC2; (b) Section of the 3-D crystal packing to show *exo*-cavity guest **9** as a bidentate hydrogen acceptor for the host hydroxyl groups in complex **9**@BrC2. The bidentate oxygen in guest molecules is marked with 'stars'.

III References

1. (a) L.-P. Zhang, W.-J. Lu and T. C. W. Mak, *Chem. Commun.*, 2003, 2830–2831; (b) N. K. Beyeh, D. P. Weimann, L. Kaufmann, C. A. Schalley and K. Rissanen, *Chem. Eur. J.*, 2012, **18**, 5552–5557;
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4. O. V Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.