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

Supporting Information

Joint experimental and theoretical studies of surprising Stability of the Aryl Pentazole upon noncovalent binding to β- cyclodextrin

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1. Supporting Experiments

Synthesis of the host-gust of carbon nanotube and **1**

β-Cyclodextrin (β-CD) (10 mg) was set in suspension in 20 mL of MeOH and CH_2Cl_2 at -35 °C. After 30 min stirring, the 5 ml dichloromethane solution of **1** (5 mg) was added dropwise during 1 min. The solution was stirred for 36 h at -50 °C. The green-grey product was obtained by filtering and vacuum drying. All glass (including filters) and solutions, used in the following work were cooled to between -60 and -50 °C by a cold bath of liquid N_2. A small amount of *p*-dimethylaminophenylazide (**2**) was produced by decomposition of **1** inevitably.

Synthesis of the host-gust of cucurbituril[6] and **1**

Cucurbituril[6] (10 mg) was set in suspension in 20 mL of MeOH and CH_2Cl_2 at -35 °C. After 30 min stirring, the 5 ml dichloromethane solution of **1** (5 mg) was added dropwise during 1 min. The solution was stirred for 36 h at -50 °C. The green-grey product was obtained by filtering and vacuum drying. All glass (including filters) and solutions, used in the following work were cooled to between -60 and -50 °C by a cold bath of liquid N_2. A small amount of *p*-dimethylaminophenylazide (**2**) was produced by decomposition of **1** inevitably. IR (KBr) ν: 3446, 2997, 2932, 1757, 1731, 1474, 1417, 1377, 1328, 1298, 1283, 1240, 1191, 967, 801, 760, 673.

Synthesis of the host-gust of calixpyrrole[4] and **1**

Calixpyrrole[4] (10 mg) was set in suspension in 20 mL of MeOH and CH_2Cl_2 at -35 °C. After 30 min stirring, the 5 ml dichloromethane solution of **1** (5 mg) was added dropwise during 1 min. The solution was stirred for 36 h at -50 °C. The green-yellow product was obtained by evaporating and vacuum drying. All glass (including filters) and solutions, used in the following work were cooled to between -60 and -50 °C by a cold bath of liquid N_2. A small amount of *p*-dimethylaminophenylazide (**2**) was produced by decomposition of **1** inevitably. IR (KBr) ν: 3443, 2971, 2928, 2870, 1662, 1519, 1385, 1348, 1230, 1041, 860, 771, 704, 565.

2. Supporting Figures

Figure S1 The DSC plot of the host-gust of carbon nanotube and **1**

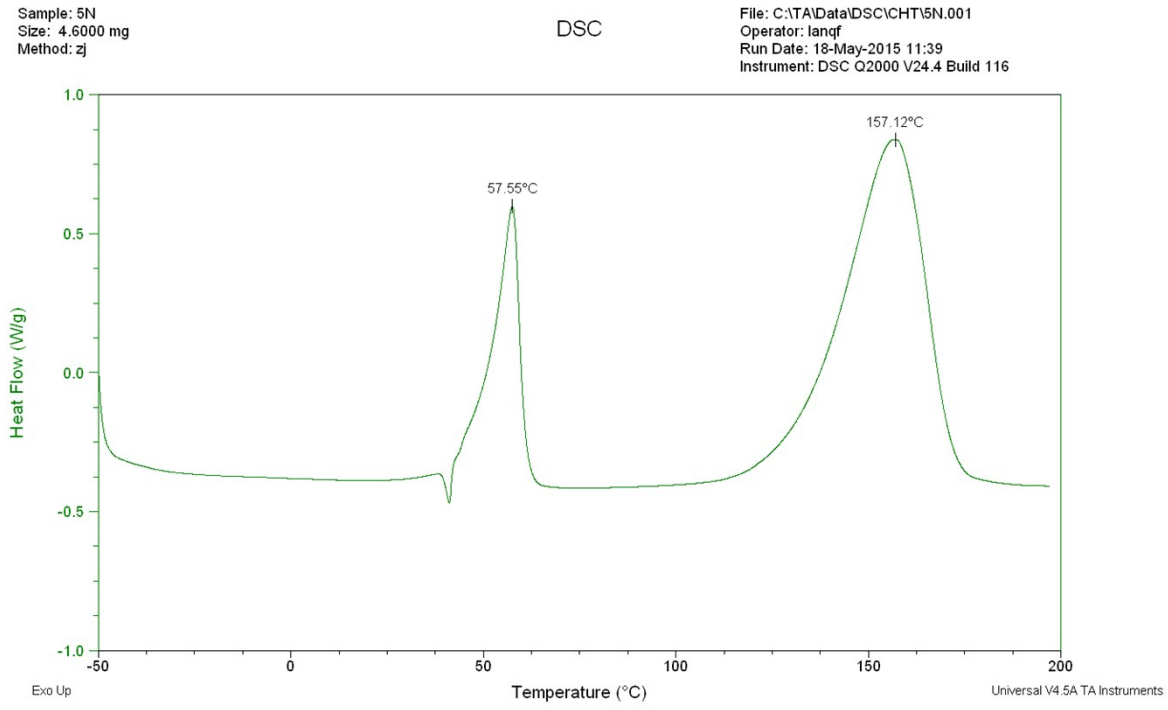


Figure S2 The DSC plot of the host-gust of cucurbituril[6] and **1**

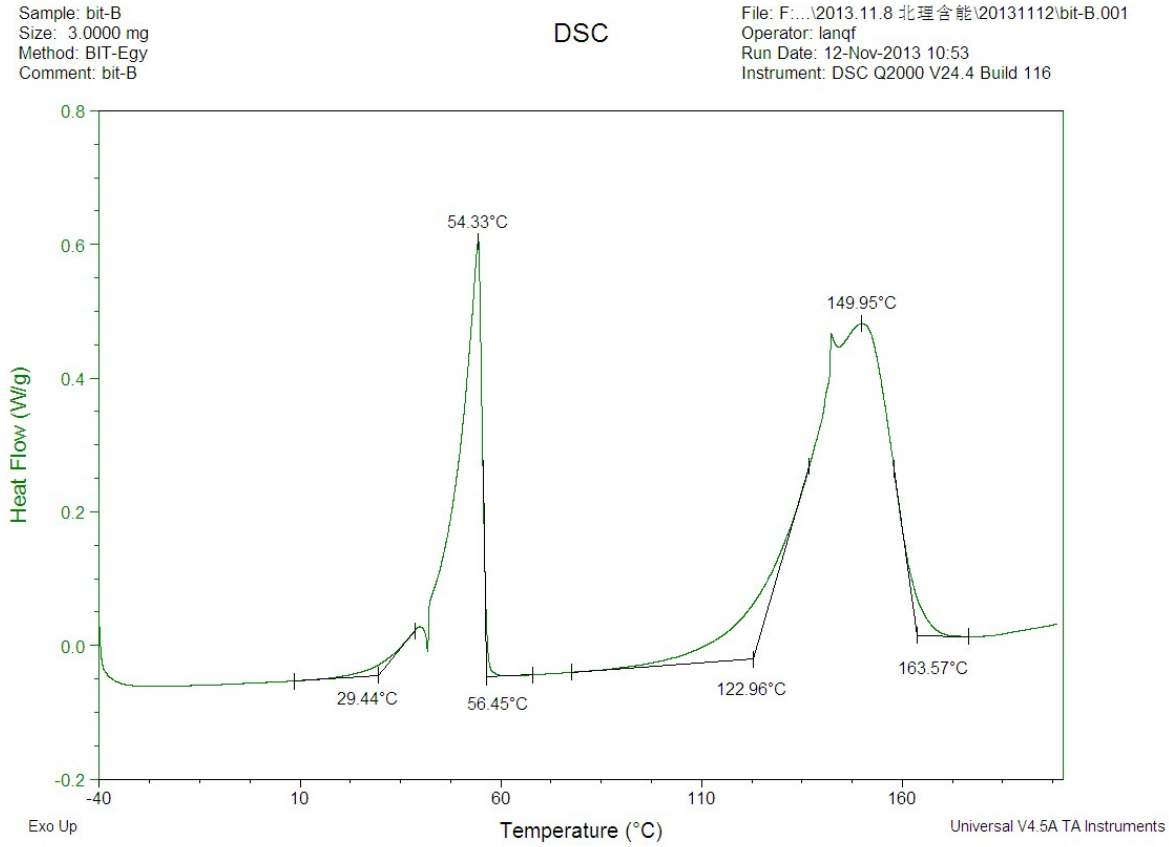


Figure S3 The DSC plot of the host-gust of calixpyrrole[4] and **1**

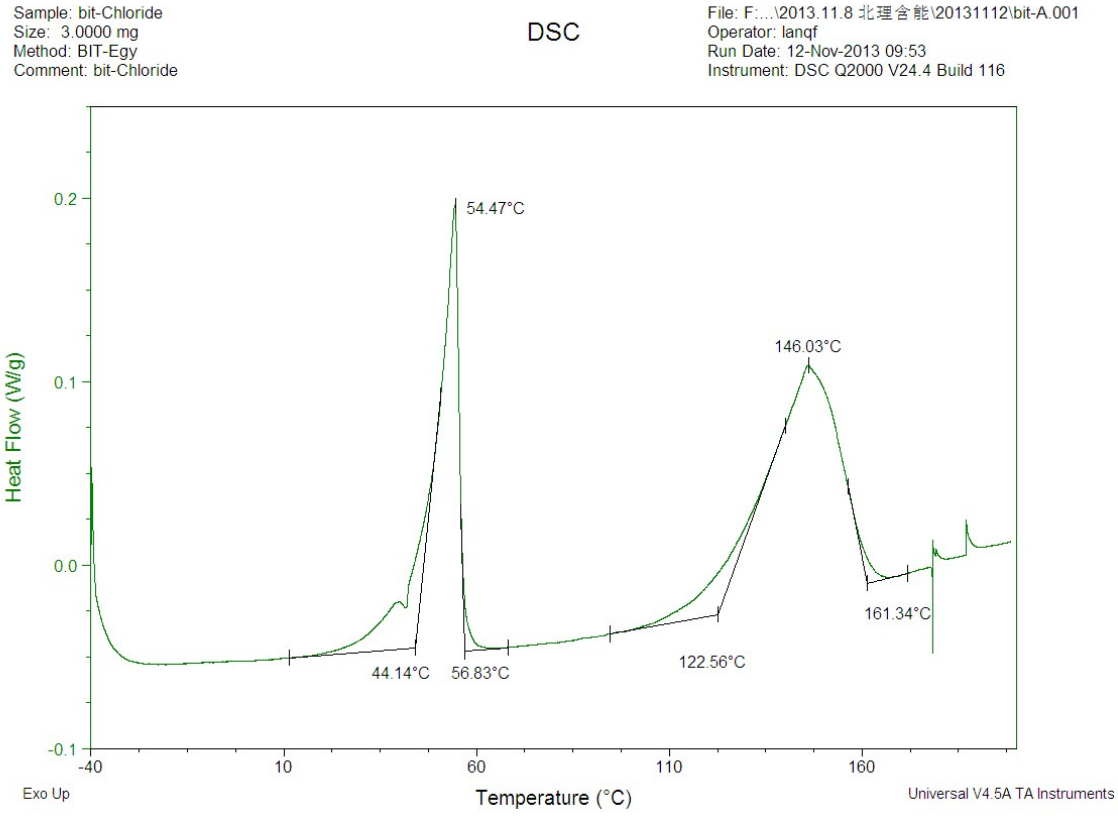
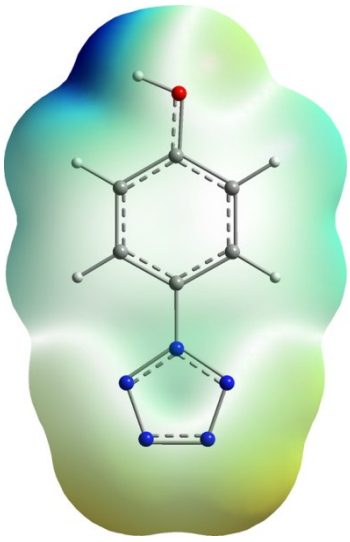
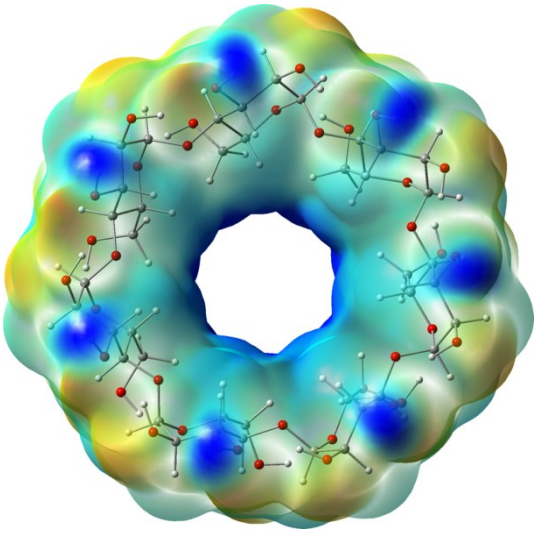


Figure S4 The molecular electrostatic potentials for the isolated aryl pentazole, β-CD and **B1**, **B2**, **B3** **B4** and **B5** complexes.



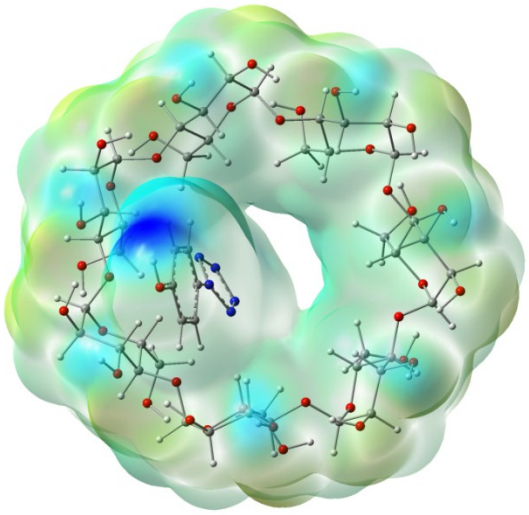


-0.101 0.101

guest

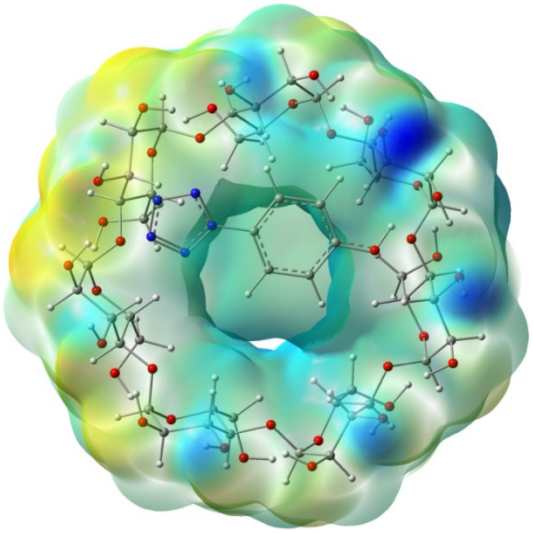
-0.070 0.070

host



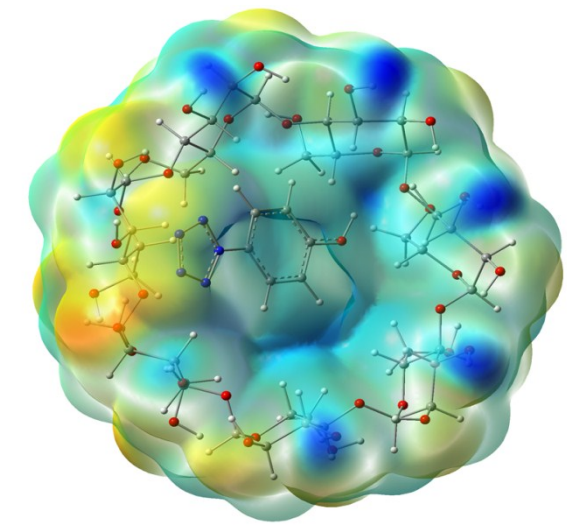
-0.116 0.116

B1



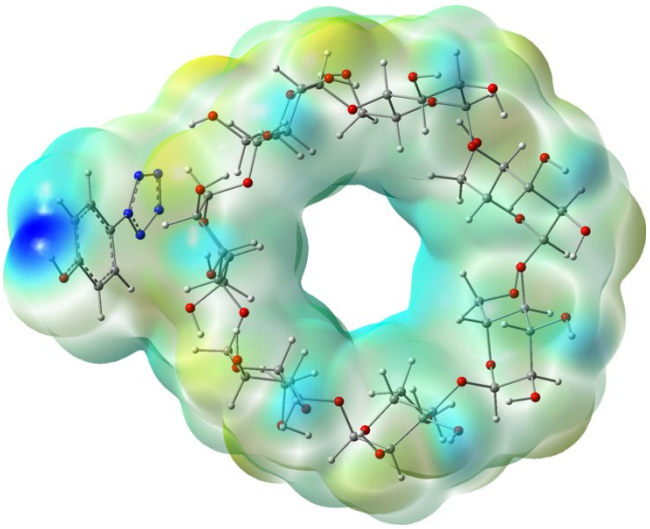
-0.091 0.091

B2



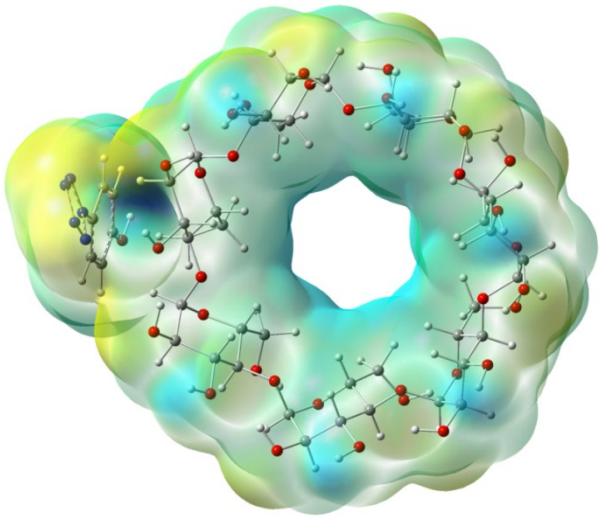
-0.078 0.078

B3



-0.107 0.107

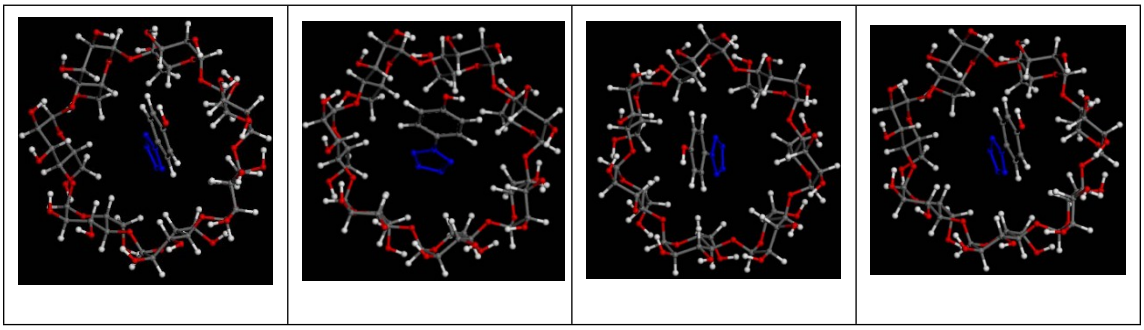
B4



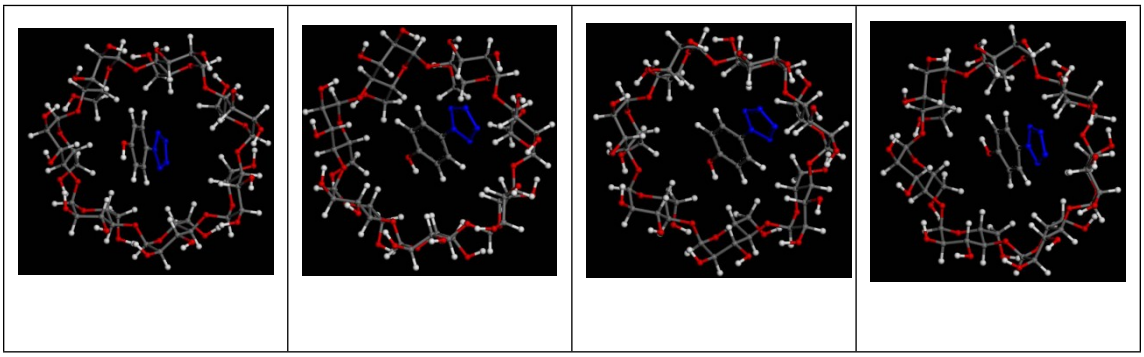
-0.105 0.105

B5

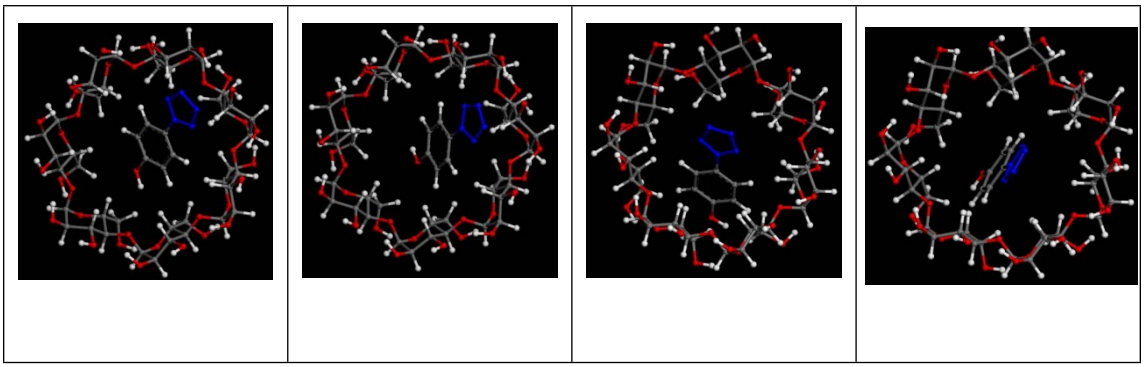
Figure S5 Monte Carlo configurations based on CVFF field. Absorption energy (in kcal mol^{-1}) in parentheses.



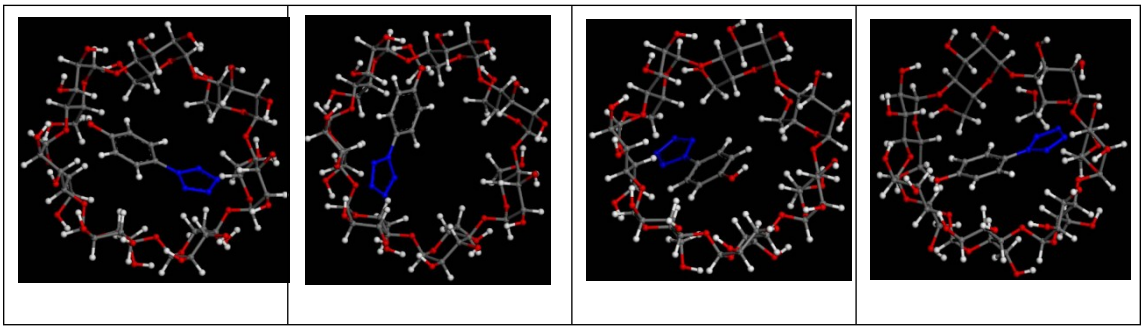
1 (-38.9) **2** (-38.7) **3** (-38.4) **4** (-38.2)



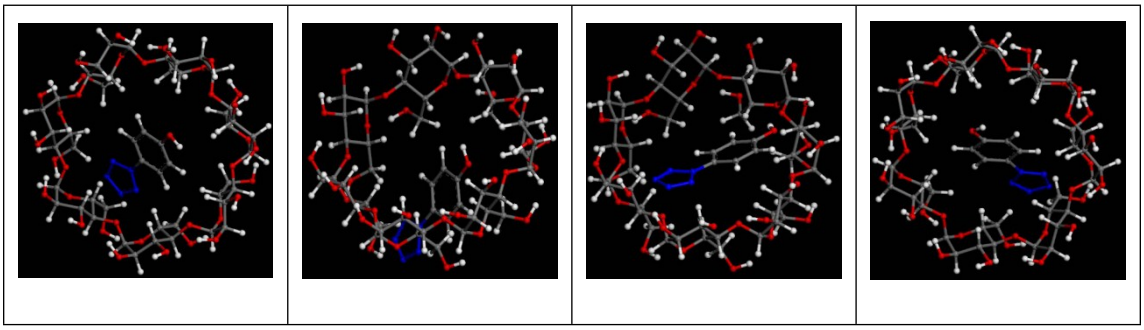
5 (-37.8) **6** (-36.7) **7** (-36.3) **8** (-36.1)



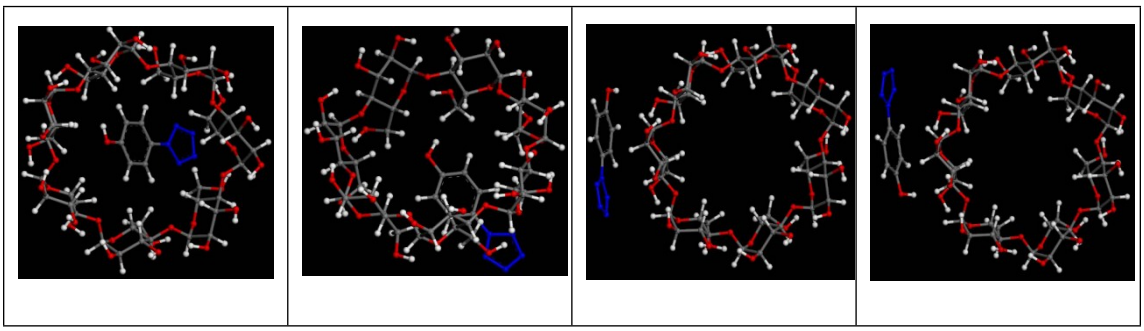
9 (-35.7) **10** (-35.3) **11** (-33.1) **12** (-32.1)



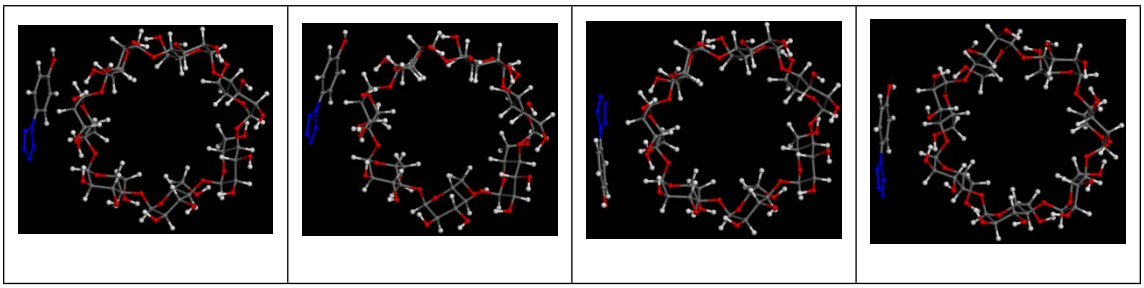
13 (-29.6) **14** (-28.3) **15** (-27.7) **16** (-27.6)



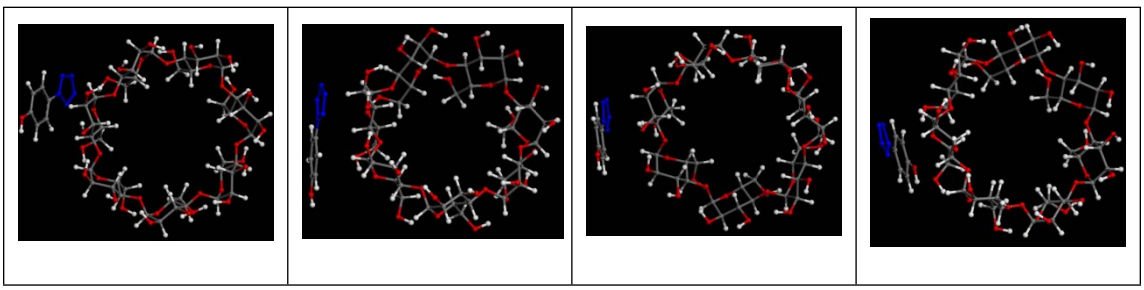
17 (-27.5) **18** (-27.2) **19** (-26.6) **20** (-26.6)



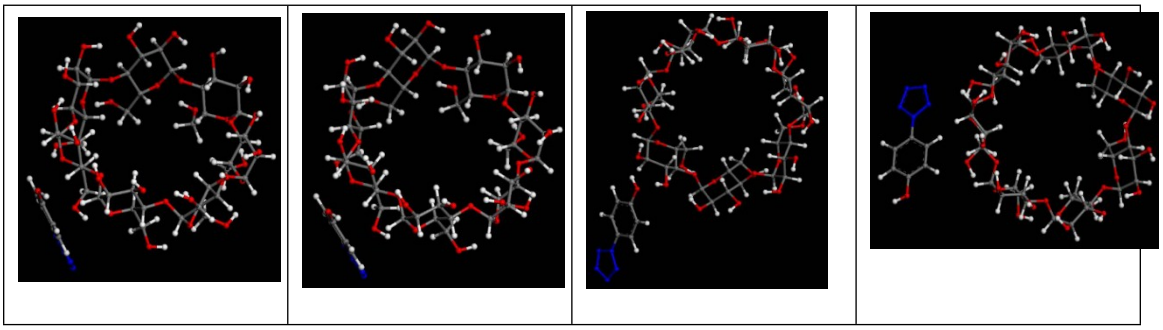
21 (-26.1) **22** (-25.7) **23** (-25.4) **24** (-25.2)



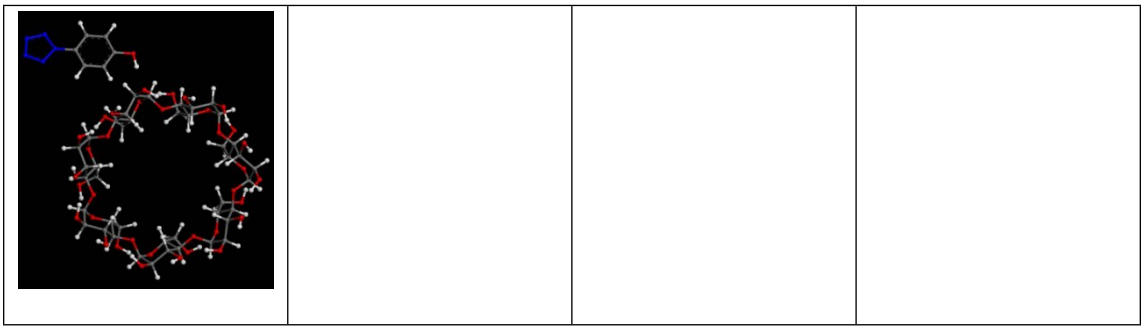
25 (-25.0) **26** (-24.7) **27** (-24.5) **28** (-24.2)



29 (-23.8) **30** (-23.6) **31** (-23.3) **32** (-22.5)

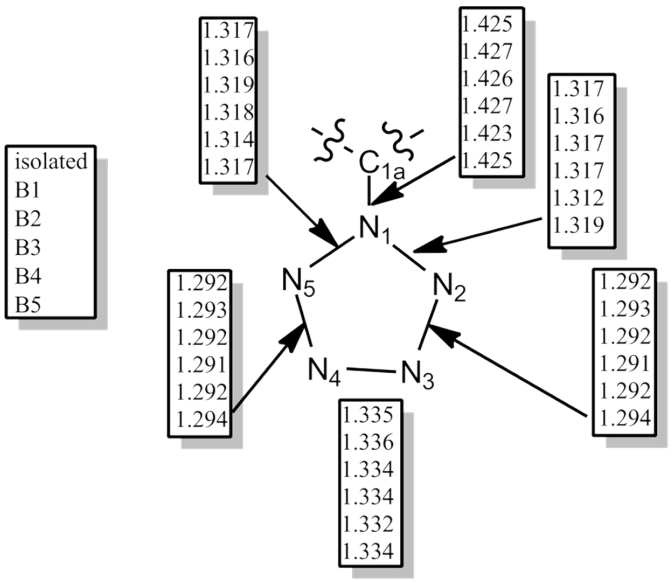


33 (-21.1) **34** (-20.9) **35** (-20.0) **36** (-19.2)

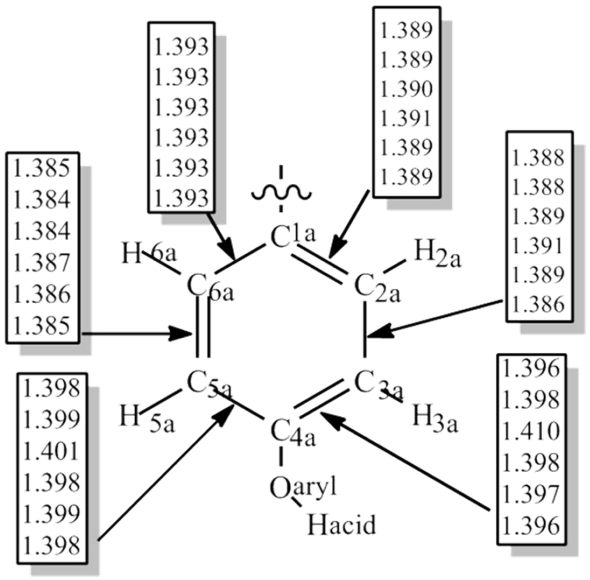


37 (-17.8)

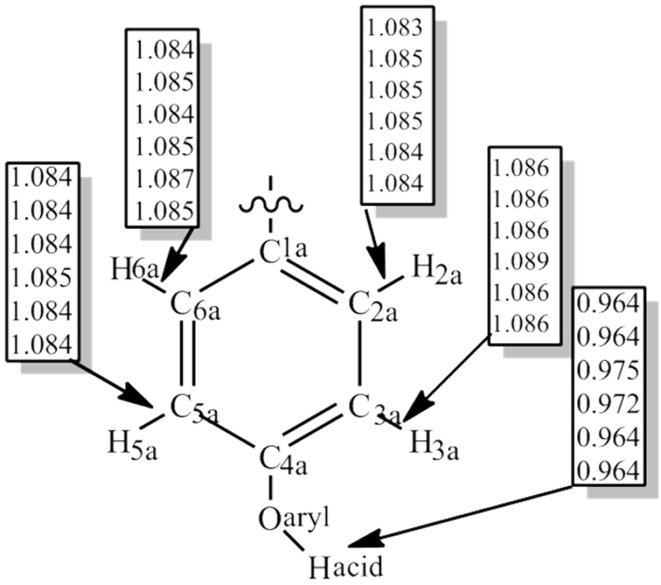
Figure S6 The (a)N-N, (b) C-C and (c) C-H bond lengths of the aryl pentazole in the isolated and the **B1-B5** host-guest complexes from top to down, respectively..


isolated
B1
B2
B3
B4
B5
1.317 1.316 1.319 1.318 1.314 1.317
1.425 1.427 1.426 1.427 1.423 1.425
1.317 1.316 1.317 1.317 1.312 1.319
1.292 1.293 1.292 1.291 1.292 1.294
1.292 1.293 1.292 1.291 1.292 1.294
1.335 1.336 1.334 1.334 1.332 1.334
C1a
N1
N2
N3
N4
N5

a

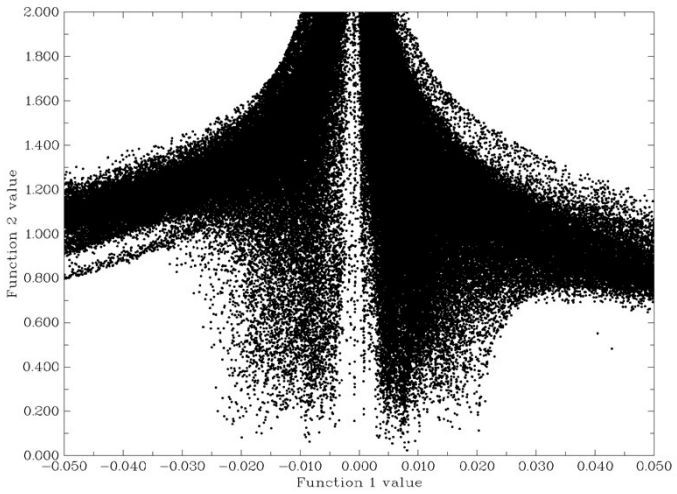

1.393 1.393 1.393 1.393 1.393 1.393
1.389 1.389 1.390 1.391 1.389 1.389
1.385 1.384 1.384 1.387 1.386 1.385
1.388 1.388 1.389 1.391 1.389 1.386
1.398 1.399 1.401 1.398 1.399 1.398
1.396 1.398 1.410 1.398 1.397 1.396
H6a
C1a
H2a
C6a
C2a
C5a
C3a
H5a
H3a
C4a
Oaryl
Hacid

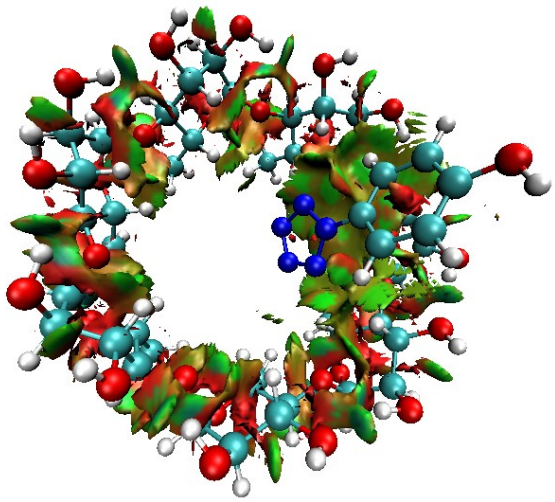
b


1.084 1.085 1.084 1.085 1.087 1.085
1.083 1.085 1.085 1.085 1.084 1.084
1.084 1.084 1.084 1.085 1.084 1.084
1.086 1.086 1.086 1.089 1.086 1.086
0.964 0.964 0.975 0.972 0.964 0.964
H6a
C1a
H2a
C6a
C2a
C5a
C3a
H5a
H3a
C4a
Oaryl
Hacid

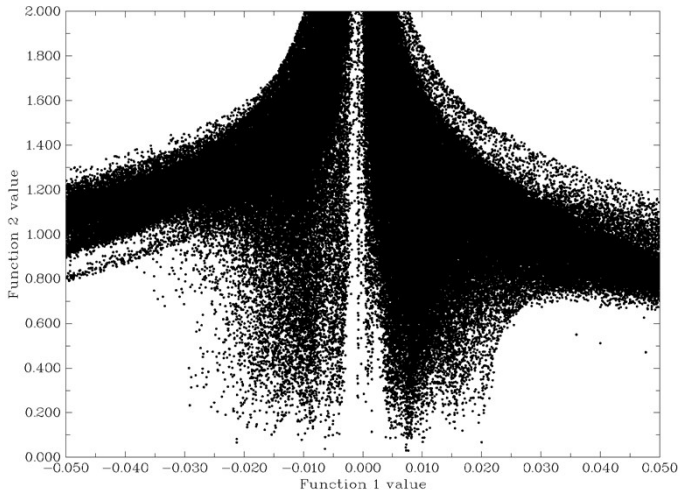
c

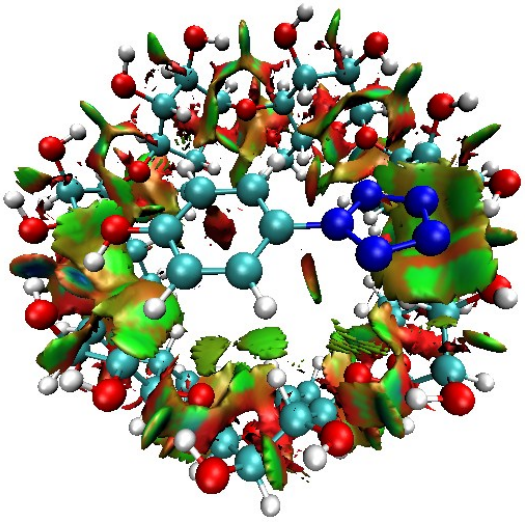
Figure S7 Color-filled RDG isosurfaces (b) depicting noncovalent interaction regions (a) in the **B1**, **B2**, **B4** and **B5** complexes. Functions 1, 2 stands for sign(λ_2)ρ and RDG/s (in au.), respectively.



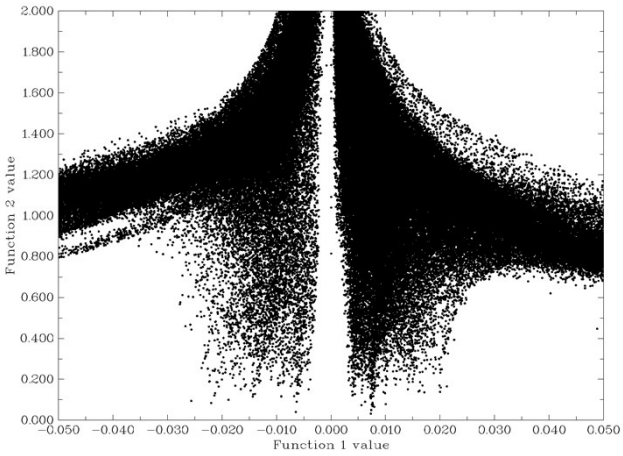


B1a **B1b**

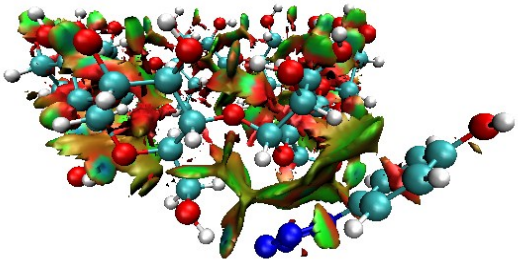




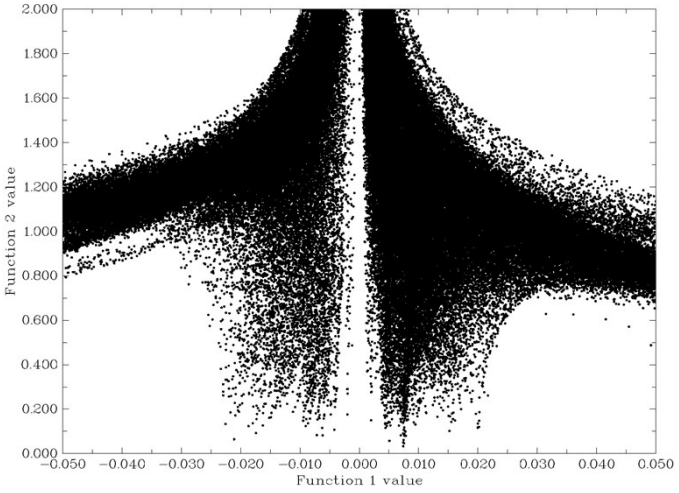
B2a **B2b**



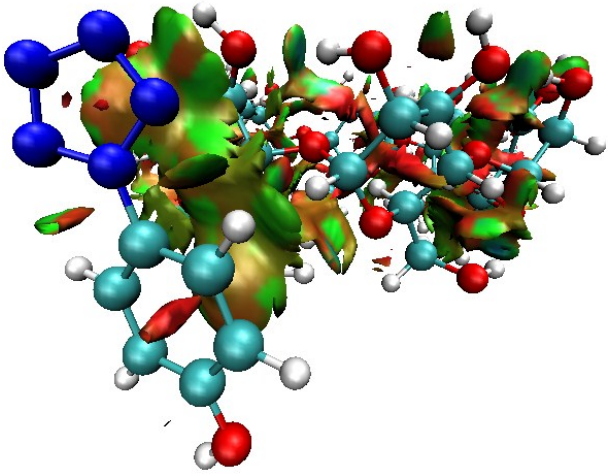
B4a



B4b

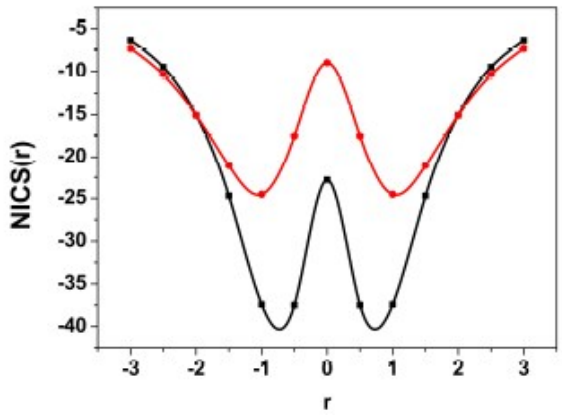


B5a

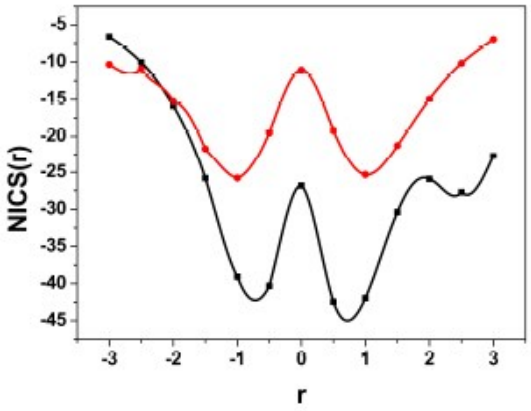


B5b

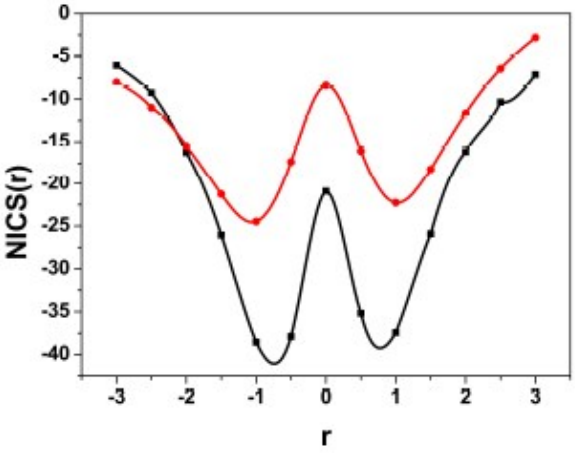
Figure S8 NICSzz values plotted as a function of distance (in Å) above and below the ring planes of the **isolated**, **B1**, **B2**, **B4** and **B5** complexes. Red is referred to the phenyl ring and black to the pentazole ring.



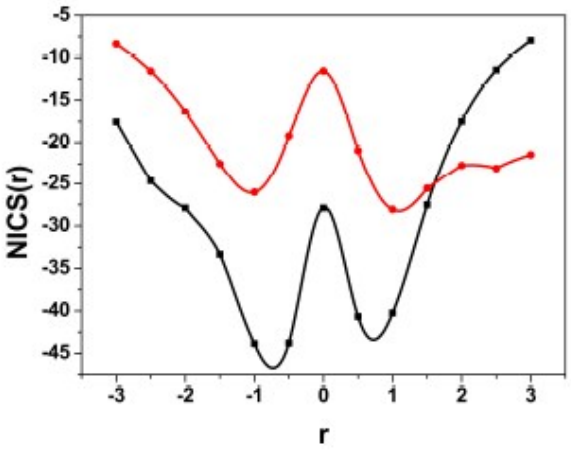
Isolated



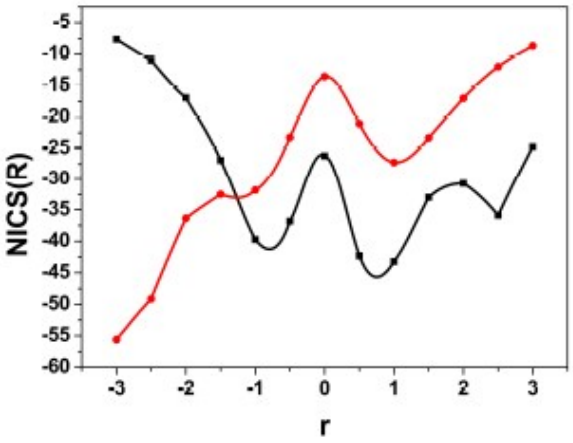
B1



B2



B4



B5

2. Supporting Tables

Table S1 Energy gaps, dipole moments and the first excited singlet energies for the isolated host, guest and their complexes.

	Guest	Host	B1	B2	B3	B4	B5
E_{HOMO}/eV	-8.29	-9.43	-8.75	-8.51	-8.79	-8.41	-8.28
E_{LUMO}/eV	-1.06	-0.99	-1.58	-1.45	-1.54	-1.14	-1.06
E_g/eV	7.23	8.44	7.17	7.06	7.25	7.27	7.22
dipole/D	6.0	2.1	7.8	7.6	4.9	6.2	3.3
λ_{S1}/nm	257	/	256	262	256	253	257

Table S2 QTAIM parameters corresponding to noncovalent interactions present in **B1**, **B2**, **B4** and **B5** inclusion complex.

For **B1**

BCP	ρ_b (×10³)	$\nabla^2\rho_b$ (×10²)	λ_2 (×10³)	G_b (×10³)	V_b (×10³)	H_b (×10³)	$-G_b/V_b$ (×10³)
N5⋯H5(C5)	8.5	3.1	-4.2	6.6	-5.5	1.1	1.20
N5⋯Obridge	8.5	2.8	-5.8	6.5	-6	0.5	1.08
N5⋯H3(C3)	6.8	2.2	-5.1	4.6	-3.8	0.8	1.21
N4⋯H5(C5)	0.79	0.3	-2.4	5.3	-3	2.3	1.77
N2⋯H3(C3)	6.7	2.1	-4.6	4.5	-3.7	0.8	1.22
N2⋯H5(C5)	9.8	3.5	-6.9	7.5	-6.3	1.2	1.19
N3⋯H5(C5)	8.7	3	-2.7	6.6	-5.7	0.9	1.16

H6a⋯H3(C3)	8	2.8	-6.8	5.8	-4.4	1.4	1.32
N4⋯H6(C6)	4.6	1.5	-1.8	3.1	-2.4	0.7	1.29
N2⋯Obridge	6.6	2.3	-4.1	5.2	-4.7	0.5	1.11
H2a⋯H3(C3)	5	1.8	-3	3.3	-2.2	1.1	1.50
C6a⋯H3(C3)	11.8	3.9	-4.8	8.2	-6.6	1.6	1.24
H6a⋯O2(H2)	9	3.1	-6.4	6.9	-6.1	0.8	1.13

For **B2**

BCP	ρ_b ($\times10^3$)	$\nabla^2\rho_b$ ($\times10^2$)	λ_2 ($\times10^3$)	G_b ($\times10^3$)	V_b ($\times10^3$)	H_b ($\times10^3$)	$-G_b/V_b$ ($\times10^3$)
N4⋯Obridge	5.1	1.8	-1.9	3.9	-3.4	0.5	1.15
N4⋯H2(O2)	10.8	3.8	-8.9	8.5	-7.4	1.1	1.15
N3⋯H3(C3)	10	3.7	-4.8	8	-6.6	1.4	1.21
N3⋯O3(H3)	12.8	5.1	-6.1	11	-9.4	1.6	1.17
N2⋯O3(H3)	0.9	0.4	-0.2	0.7	-0.4	0.3	1.75
N5⋯H3(C3)	6.4	2.3	-3.7	4.9	-3.8	1.1	1.29
C3a⋯H3(C3)	10.4	3.8	-4.2	7.5	-5.8	1.7	1.29
H2a⋯H3(C3)	4.4	1.5	-2.2	2.8	-1.8	1	1.56
H3a⋯O3(H3)	11	3.6	-9.6	8.5	-8	0.5	1.06
H5a⋯H3(C3)	0.8	0.3	-5.1	0.5	-0.3	0.2	1.67
H6a⋯H3(C3)	0.3	0.1	-0.2	0.2	-0.1	0.1	2.00
Hacid⋯O2(2)	25.9	7.6	-32	19.8	-20.6	-0.8	0.96
Oaryl⋯Obridge	7.3	2.6	-4.1	6	-5.7	0.3	1.05
Oaryl⋯H3(C3)	11	3.9	-10.2	8.8	-8	0.8	1.10
Oaryl⋯H3'(C3')	8.6	3.6	-2.8	7.4	-5.7	1.7	1.30

For **B3**

BCP	ρ_b ($\times10^3$)	$\nabla^2\rho_b$ ($\times10^2$)	λ_2 ($\times10^3$)	G_b ($\times10^3$)	V_b ($\times10^3$)	H_b ($\times10^3$)	$-G_b/V_b$ ($\times10^3$)
N1···$H3_a(C3_a)$	9.7	3.4	-1.6	7.6	-6.5	1.1	1.17
N4···O3(H3)	7.4	3.0	-3.5	6.2	-5.0	1.2	1.24
N3···O2(H2)	12.1	4.5	-4.7	10.0	-8.7	1.3	1.15
N5···$H3_b(C3_b)$	11.3	3.6	-10.3	8.0	-6.9	1.1	1.16
H_{2a}···O_{bridge}	4.0	1.5	-1.4	2.9	-2.2	0.7	1.32
H_{2a}···$H3_a(C3_a)$	8.0	3.0	-6.7	5.8	-4.3	1.5	1.35
H_{3a}···$O_{bridge(1\ or\ 4)}$	9.7	3.2	-8.8	7.5	-7.0	0.5	1.07
H_{3a}···$H5_a(C5_a)$	4.1	1.4	-0.8	2.6	1.8	4.4	1.44
H_{3a}···$H3_c(C3_c)$	6.0	2.0	-4.1	3.9	-2.8	1.1	1.39
H_{3a}···$H5_b(C5_b)$	3.8	1.2	-0.6	2.3	-1.7	0.6	1.35
H_{3a}···$H3_d(C3_d)$	5.7	2.1	-2.4	4.1	-2.9	1.2	1.41
H_{5a}···$H5_c(C5_c)$	0.9	0.3	-0.4	0.5	-0.3	0.2	1.67
H_{5a}···$H5_d(C5_d)$	1.1	0.4	-0.6	0.6	-0.4	0.2	1.50
H_{6a}···$H3_e(C3_e)$	0.9	0.3	-0.4	0.5	-0.3	0.2	1.67
H_{acid}···$O_{bridge(1\ or\ 4)}$	20.8	6.5	-23.6	17.0	-17.7	-0.7	0.96
H_{acid}···$H5_b(C5_b)$	9.5	3.7	-6.0	7.8	-6.3	1.5	1.24
O_{aryl}···$H3_f(C3_f)$	5.4	1.9	-3.1	4.0	-3.2	0.8	1.25
O_{aryl}···$H5_e(C5_e)$	11.2	4.0	-10.2	9.2	-8.3	0.9	1.11

For **B4**

BCP	ρ_b ($\times10^3$)	$\nabla^2\rho_b$ ($\times10^2$)	λ_2 ($\times10^3$)	G_b ($\times10^3$)	V_b ($\times10^3$)	H_b ($\times10^3$)	$-G_b/V_b$ ($\times10^3$)
N1···O_{bridge}	14.7	5.5	-9.7	12.8	-11.9	0.9	1.08
N3···H6(O6)	22.2	7.1	-24.9	17.4	-17.1	0.3	1.02
N2···H1(C1)	8.9	3.1	-6.3	6.6	-5.5	1.1	1.20
N5···O6(H6)	6.8	2.4	-4.1	5.5	-5.0	0.5	1.10
N5···H6(C6)	6.5	2.3	-1.4	4.8	-3.8	1.0	1.26
C_{1a}···H2(C2)	6.4	2.0	-1.7	4.1	-3.2	0.9	1.28
C_{6a}···H4(C4)	7.5	2.4	-3.9	4.9	-3.8	1.1	1.29
H_{6a}···O6(H6)	15.2	4.8	-15.2	11.9	-11.8	0.1	1.00

For **B5**

BCP	ρ_b ($\times10^3$)	$\nabla^2\rho_b$ ($\times10^2$)	λ_2 ($\times10^3$)	G_b ($\times10^3$)	V_b ($\times10^3$)	H_b ($\times10^3$)	$-G_b/V_b$ ($\times10^3$)
N2···H2(C2)	8.6	3.1	-1.4	6.9	-5.9	1	1.17
N5···O3(H3)	9.5	3.2	-3	7.4	-6.9	0.5	1.07
N5···H4(C4)	7.2	2.5	-2.7	5.3	-4.5	0.8	1.18
C1a···H4(C4)	6.9	2.3	-2.6	4.8	-3.8	1	1.26

C2a⋯Oring	2	0.7	-0.3	1.4	-0.9	0.5	1.56
C4a⋯O6(H6)	8.4	2.9	-1.6	6.3	-5.4	0.9	1.17
C6a⋯H5(C5)	6.1	1.9	-3.5	3.8	-2.8	1	1.36

Table S3 The selected charge transfer energies for the B3 complex from NBO calculations.

$LP_{N1}\rightarrow \sigma^*_{C3a\text{-}H3a}$	0.22	$\sigma_{C2a-H2a}\rightarrow RY^*_{Obridge}$	0.32	$\sigma_{C3a\text{-}H3a}\rightarrow \sigma^*_{C5b\text{-}H5b}$	0.18
$LP_{N2}\rightarrow \sigma^*_{C3a'\text{-}H3a}$	0.42	$\sigma_{C2a-H2a}\rightarrow \sigma^*_{C3a\text{-}H3a}$	0.14	$\sigma_{Oaryl\text{-}Hacid}\rightarrow RY^*_{Obridge}$	2.06
$LP_{N3}\rightarrow \sigma^*_{O3\text{-}H3}$	0.60	$\sigma_{C3a-H3a}\rightarrow RY^*_{Obridge}$	1.33	$\sigma_{Oaryl\text{-}Hacid}\rightarrow RY^*_{H5b}$	0.17
$LP_{N4}\rightarrow \sigma^*_{O2\text{-}H2}$	0.36	$\sigma_{C3a\text{-}H3a}\rightarrow RY^*_{H3c}$	0.18	$\sigma_{Oaryl\text{-}Hacid}\rightarrow \sigma^*_{C5b\text{-}H5b}$	0.59
$LP_{N5}\rightarrow \sigma^*_{C3b\text{-}H3b}$	2.56	$\sigma_{C3a\text{-}H3a}\rightarrow \sigma^*_{C3c\text{-}H3c}$	0.40	$LP_{Oaryl}\rightarrow \sigma^*_{C5e\text{-}H5e}$	0.82
$\pi_{N4\text{-}N5}\rightarrow \sigma^*_{O2\text{-}H2}$	0.94	$\sigma_{C3a\text{-}H\ 3a}\rightarrow \sigma^*_{C5a\text{-}H5a}$	0.10	$LP_{Obridge}\rightarrow \sigma^*_{Oaryl\text{-}Hacid}$	7.63
$\pi_{N3\text{-}N2}\rightarrow \sigma^*_{O3\text{-}H3}$	0.61	$\sigma_{C3a\text{-}H3a}\rightarrow \sigma^*_{C3d\text{-}H3d}$	0.28	$\sigma_{C5b\text{-}H5b}\rightarrow \sigma^*_{Oaryl\text{-}Hacid}$	0.89

Table S4 NMR chemical shifts (ppm) of the isolated host, guest and the **B3** complex calculated in CH_2Cl_2 solvent at the Wb97xd/ 6-31+G(d,p) and M06-2X/ 6-31+G(d,p) levels.

For **Wb97xd/ 6-31+G(d,p)**

guest-host	host [a]	host [b]	guest	guest [a]	guest [b]
$N1\cdots H3_a(C3_a)$	4.19	2.94	C_{1a}	110.5	112.5
$N5\cdots H3_b(C3_b)$	4.21	5.26	C_{2a}	105.7	108.6
$H_{2a}\cdots O_{bridge}$			C_{3a}	97.8	101
$H_{2a}\cdots H3_a(C3_a)$	4.19	2.94	C_{4a}	141	142.2
$H_{3a}\cdots O_{bridge}$			C_{5a}	99.9	102.8
$H_{3a}\cdots H5_a(C5_a)$	4.38	4.49	C_{6a}	106	108
$H_{3a}\cdots H3_c(C3_c)$	4.13	4.71	N1	290.9	291.4
$H_{3a}\cdots H5_b(C5_b)$	4.33	4.40	N2	339.2	341.4

$H_{3a}\cdots H3_d(C3_d)$	4.28	4.91	N3	372.4	374
$H_{5a}\cdots H5_c(C5_c)$	4.44	4.53	N4	372.4	377
$H_{5a}\cdots H5_d(C5_d)$	4.26	4.66	N5	339.2	342.1
$H_{6a}\cdots H3_e(C3_e)$	4.2	4.47	H_{2a}	8.99	9.3
$H_{acid}\cdots O_{bridge}$			H_{3a}	7.31	7.86
$H_{acid}\cdots H5_b(C5_b)$	4.33	4.4	H_{5a}	7.67	7.86
$O_{aryl}\cdots H3_f(C3_f)$	4.25	4.7	H_{6a}	9.04	9.13
$O_{aryl}\cdots H5_e(C5_e)$	5.02	4.23	H_{acid}	5.31	6.59

For **M06-2X/ 6-31+G(d,p)**

guest-host	host [a]	host [b]	guest	guest [a]	guest [b]
$N1\cdots H3_a(C3_a)$	3.94	2.99	C_{1a}	122.7	123.8
$N5\cdots H3_b(C3_b)$	4.24	5.09	C_{2a}	119	123.4
$H_{2a}\cdots O_{bridge}$			C_{3a}	111.9	115.7
$H_{2a}\cdots H3_a(C3_a)$	3.94	2.99	C_{4a}	156	157
$H_{3a}\cdots O_{bridge}$			C_{5a}	113.9	117.8
$H_{3a}\cdots H5_a(C5_a)$	3.81	2.94	C_{6a}	119.6	121
$H_{3a}\cdots H3_c(C3_c)$	4.14	3.53	N1	320.6	320.2
$H_{3a}\cdots H5_b(C5_b)$	3.78	4.01	N2	385.4	394
$H_{3a}\cdots H3_d(C3_d)$	4.3	5.16	N3	419.2	420.8
$H_{5a}\cdots H5_c(C5_c)$	3.97	4.18	N4	419.2	428.8
$H_{5a}\cdots H5_d(C5_d)$	3.77	4.04	N5	385.3	391.3
$H_{6a}\cdots H3_e(C3_e)$	4.43	4.81	H_{2a}	9.45	9.81
$H_{acid}\cdots O_{bridge}$			H_{3a}	7.76	8.39
$H_{acid}\cdots H5_b(C5_b)$	3.78	4.01	H_{5a}	8.07	8.58
$O_{aryl}\cdots H3_f(C3_f)$	3.89	4.93	H_{6a}	9.49	9.77
$O_{aryl}\cdots H5_e(C5_e)$	3.52	4.23	H_{acid}	5.69	7.08

[a] in the isolated and [b] in the host-guest complex.

the subscripts with the host stands for the different atoms. The benchmark values for δ_H= 31.8821, δ_C=182.4656 ppm from TMS; δ_N=258.4 ppm from NH_3, which were calculated at the B3LYP/6-311+G(2d, p) level.

Table S5 NMR chemical shifts (ppm) of the isolated host and the **B1**, **B2**, **B4** and **B5** complexes in CH_2Cl_2 solvent at the M06-2X/ 6-31+G(d,p) level.

For **B1**

guest-host	Host	Guest	complex	Guest	complex
N5···H5(C5)	3.52		4.51	C1a	126.2
N5···H3(C3)	3.89		5.49	C2a	120.7
N4···H5(C5)	3.78		3.86	C3a	113.8
N4···H6(C6)	4.07		2.85	C4a	157.1
N2···H3(C3)	4.43		5.23	C5a	116.2
N2···H5(C5)	3.97		3.99	C6a	125.3
N3···H5(C5)	3.77		-0.61	N1	320.9
H6a···H3(C3)	3.89	9.49	9.67/5.49	N2	394.1
H2a···H3(C3)	4.43	9.25	9.45/5.23	N3	422.1
C6a···H3(C3)	3.94		9.67	N4	422.2
				N5	391.9

For **B2**

guest-host	host	guest	complex	guest	complex
N4···H2(O2)	3.99		4.63	C1a	120.5
N3···H3(C3)	4.43		1.3	C2a	118.9
N5···H3'(C3')	3.94		5.04	C3a	113.7
C3a···H3(C3)	3.94		4.42	C4a	158

H2a···H3(C3)	4.24	9.45	9.43/4.18	C5a	116
H3a···O3(H3)	7.76		8.34	C6a	119.6
H5a···H3(C3)	8.07	4.14	8.29/4.83	N1	320.5
H6a···H3(C3)	9.49	3.89	9.58/4.39	N2	402.6
Hacid···O2(H2)	5.69		8.07	N3	402.4
Oaryl···H3(C3)		4.3	4.54	N4	425.7
Oaryl···H3(C3)		3.94	4.42	N5	377.5

For **B4**

guest···host	host	complex	guest	complex
N3···H6(O6)	3.08	3.90	C_{1a}	157.1
N2···H1(C1)	5.03	4.15	C_{2a}	110.0
N5···H6(C6)	3.88	4.02	C_{3a}	121.5
C_{1a}···H2(C2)	3.35	1.51	C_{4a}	123.1
C_{6a}···H4(C4)	3.80	3.90	C_{5a}	122.3
H_{6a}···O6(H6)	9.49	10.84	C_{6a}	116.1
			N1	320.5
			N2	385.4
			N3	412.4
			N4	420.8
			N5	402.8

For **B5**

guest-host	host	guest	complex	host	complex
N2···H2(C2)	3.35		0.6	C1a	122.5
N5···H4(C4)	3.8		2.67	C2a	125.9
C1a···H4(C4)	3.8		2.67	C3a	113.7
C6a···H5(C5)	4.89		4.58	C4a	158.9
				C5a	114.7

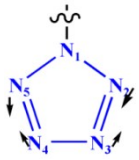
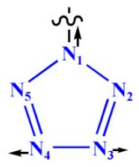
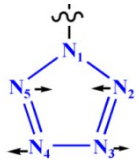
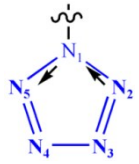
	C6a	119.1
	N1	322.3
	N2	398.1
	N3	414.8
	N4	425.8
	N5	398.4

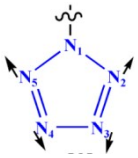
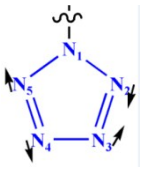
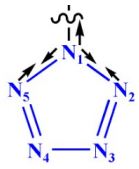
Table S6 The relative energies (kcal mol^{-1}) along the decomposition paths of the aryl pentazole in the host-guest complexes.The data under consideration of the bulky CH2Cl2 solvent are put in the parentheses.

	Initial	TS1	IM1	TS2	Product
			B1		
$\Delta(E_0+ZPE)$	0	40.0 (41.3)	35.3 (36.4)	41.1 (41.6)	-26.5 (-24.2)
ΔH	0	40.3	36.1	41.8	-24.5
ΔG	0	39.9	34.9	40.5	-29.1
			B2		
Δ(E0+ZPE)	0	39.5 (40.7)	35.6 (36.5)	41.5 (41.5)	-26.4 (-24.2)
ΔH	0	40.0	36.1	42.5	-24.1
ΔG	0	39.5	36.1	40.9	-29.8
			B3		
$\Delta(E_0+ZPE)$	0	38.3 (39.8)	34.0 (35.1)	37.8 (39.2)	-27.1 (-24.3)
ΔH	0	38.8	34.6	38.5	-25.3
ΔG	0	37.2	33.5	37.3	-29.3
			B4		
$\Delta(E_0+ZPE)$	0	41.6 (42.3)	37.8 (37.5)	44.6 (43.9)	-23.1 (-21.3)
ΔH	0	42.0	38.7	45.6	-21.0
ΔG	0	40.4	36.0	43.1	-26.5

		B5			
$\Delta(E_0+ZPE)$	0	37.0 (39.3)	32.4 (33.5)	37.2 (38.4)	-28.6 (-26.9)
ΔH	0	37.1	32.9	37.7	-26.7
ΔG	0	37.9	32.5	37.6	-30.6

Table S7 Vibration frequencies for the pentazole ring of the isolated aryl pentazole and the host-guest complexes **B1**~**B5**.

	modes	guest	B1	B2	B3	B4	B5
vibration 1		1055	1062	1061	1054	1074	1056
IR		60	16	44	56	71	21
Raman		45	21	28	26	28	21
vibration 2		1106	1107	1108	1106	1117	1105
IR		11	13	135	61	10	31
Raman		14	13	8	13	4	11
vibration 3		1215	1214	1213	1210	1220	1208
IR		27	2	1	9	8	9
Raman		5	6	5	2	2	4
vibration 4		1227	1225	1224	1230	1241	1227
IR		4	223	73	2	4	346
Raman		1	0.9	2	1	0	3

vibration 5		1326	1329	1338	1327	1341	1319
IR		36	41	23	52	64	18
Raman		7	10	6	7	6	7
vibration 6		1456	1451	1458	1451	1458	1450
IR		8	8	25	9	16	1
Raman		14	5	35	11	2	2
vibration 7		**1469**	**1467**	**1467**	**1465**	**1476**	**1469**
IR		12	38	25	8	18	23
Raman		**315**	**211**	**299**	**181**	**162**	**196**

4. Notes on **the O_{aryl}-H_{acid}···H5-C5 interaction details**

The NPA charges of the H_{acid} and the H5 are + 0.538 and + 0.220 e in the host-guest complex, respectively. In their isolated states, they are + 0.519 and + 0.239 e, respectively. The O_{aryl}–H_{acid} bond length is 0.972 Å, which is a bit longer than the counterpart 0.964 Å of the isolated guest but close to the average value 0.975 Å of the O-H bonds as the hydrogen bonding donor in the larger

open end of the β-CD. The H5-C5 bond length is 1.101 Å, which is unchanged when compared to the corresponding bond length in the isolated β-CD. The elongated O_{aryl}-H_{acid} bond should be attributed to the CT effects, mainly from its adjacent LP(O_{bridge}) and σ_{C5H5} to $\sigma^*O_{aryl}H_{acid}$, and their CT energies are 7.63 and 0.89 kcal mol^{-1}, respectively. The special H···H interaction could be stabilized by charge transfer of the $\sigma_{OarylHacid} \rightarrow \sigma^*_{C5H5}$, whose second perturbation energy is 0.59 kcal mol^{-1}; in turn the $\sigma_{C5H5} \rightarrow \sigma^*_{Oaryl}$ energy is ca. 0.89 kcal mol-1.