Supplementary Information:

Crystal Data

Crystal data for C-hexyltetracyanoresorcin[4]arene: $C_{59}H_{82}N_4O_{12}$, M = 1038, orange prism, 0.50 × 0.35 × 0.20 mm^3, monoclinic, space group $P\ 2_1/n$ (No. 14), V = 5879(3) Å^3, Z = 4, D_c = 1.1741 g/cm^3, F_{000} = 2240, Bruker APEXII CCD area detector, MoKα radiation, λ = 0.71073 Å, T = 173(2)K, $2\theta_{max}$ = 55.0º, 68252 reflections collected, 13444 unique (R_{int} = 0.0376). Final *GooF* = 1.037, *R1* = 0.0572, *wR2* = 0.1582, *R* indices based on 10357 reflections with I >2sigma(I) (refinement on F^2), 753 parameters, 3 restraints. Lp and absorption corrections applied, μ = 0.082 mm^{-1}.

Crystal data for C-hexyltetracyanoresorcin[4]arene/Ag: $C_{59.60}H_{82}AgN_4O_{11.90}$, M = 1152.76, yellow rod, .25 × .25 × .15 mm^3, orthorhombic, space group $P\ 2_1\ 2_1\ 2_1$ (No. 19), V = 6650.6(13) Å^3, Z = 4, D_c = 1.151 g/cm^3, F_{000} = 2439, Bruker APEXII CCD area detector, MoKα radiation, λ = 0.71073 Å, T = 173(2)K, 77688 reflections collected, 15196 unique (R_{int} = 0.0467). Final *GooF* = 1.119, *R1* = 0.1058, *wR2* = 0.2857, *R* indices based on 8239 reflections with I >2sigma(I) (refinement on F^2), 670 parameters, 50 restraints. Lp and absorption corrections applied, μ = 0.359 mm^{-1}.

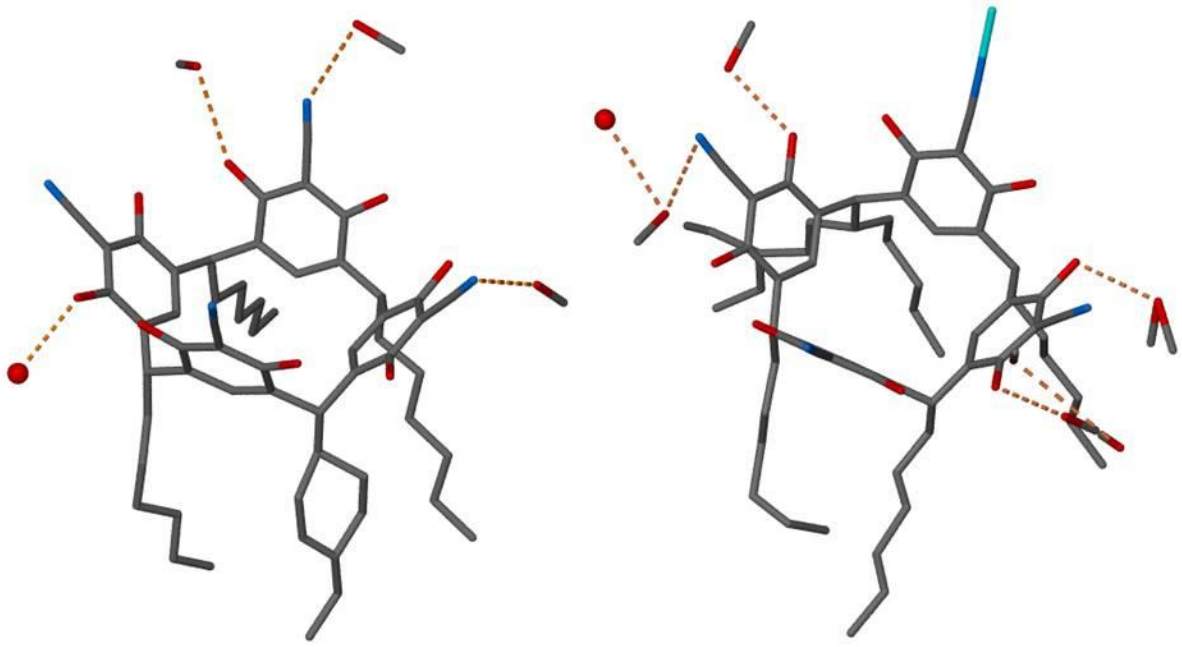

Figure 1: Asymmetric units of compound 1 (left) and 2 (right)

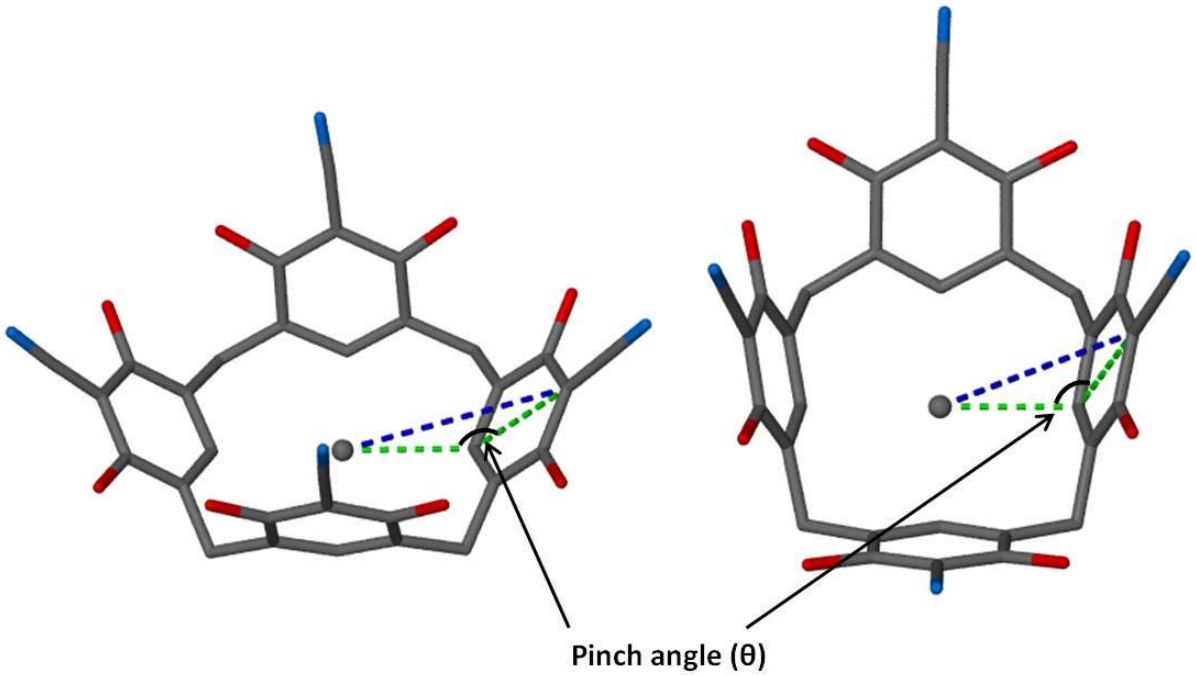

Figure 2: Two generalized views displaying pinch angle in cmpds 1 and 2

Angle containing	Pinch Angle (°)	
	cmpd 1	cmpd 2
C1	112.12	118.1
C8	140.54	135.25
C15	110.63	120.57
C22	136.34	136.01

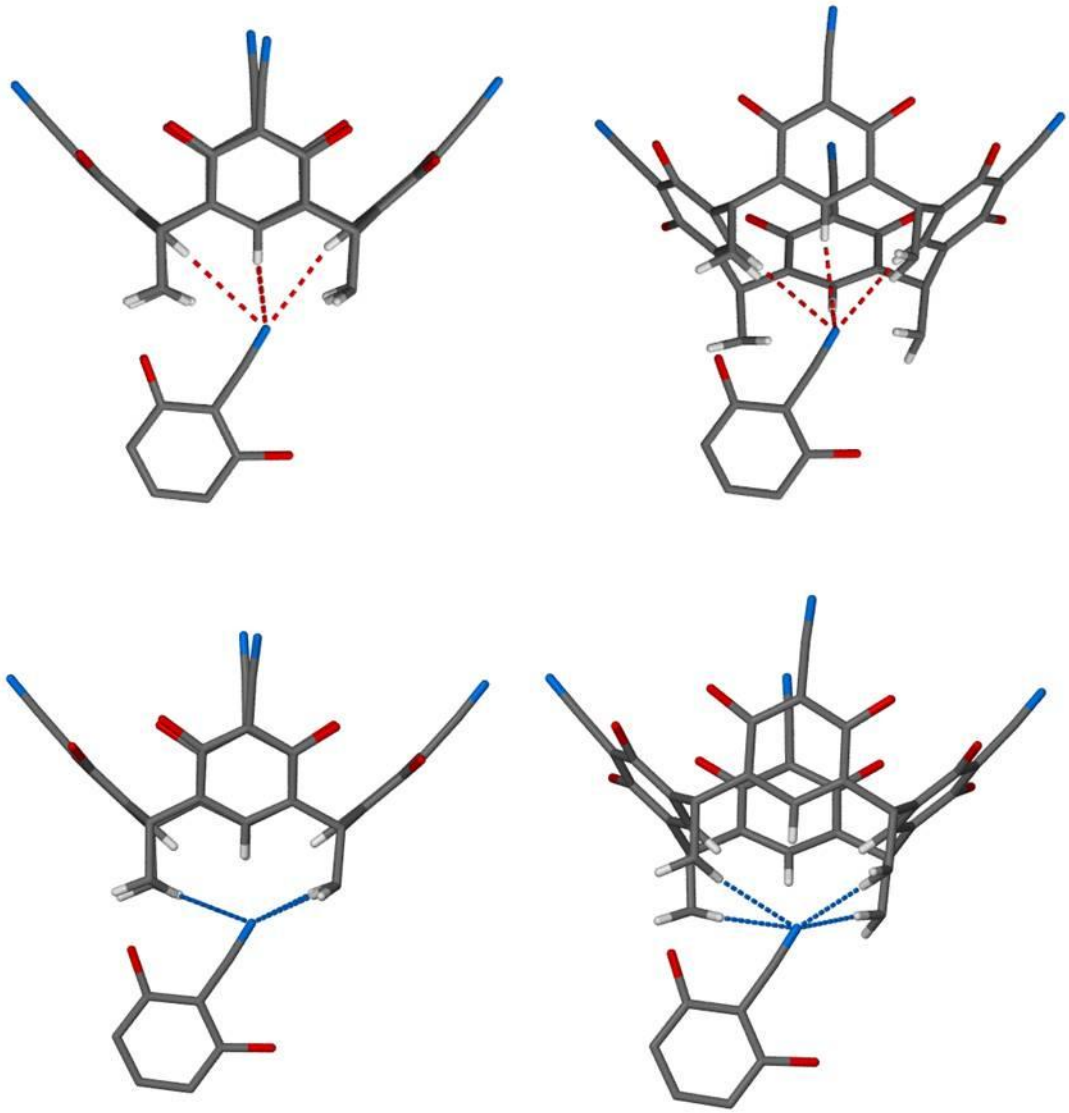

Figure 3: Two generalized views displaying CH(sp2)N interactions (top) and CH(sp3)N interactions (bottom) in cmpds 1 and 2.

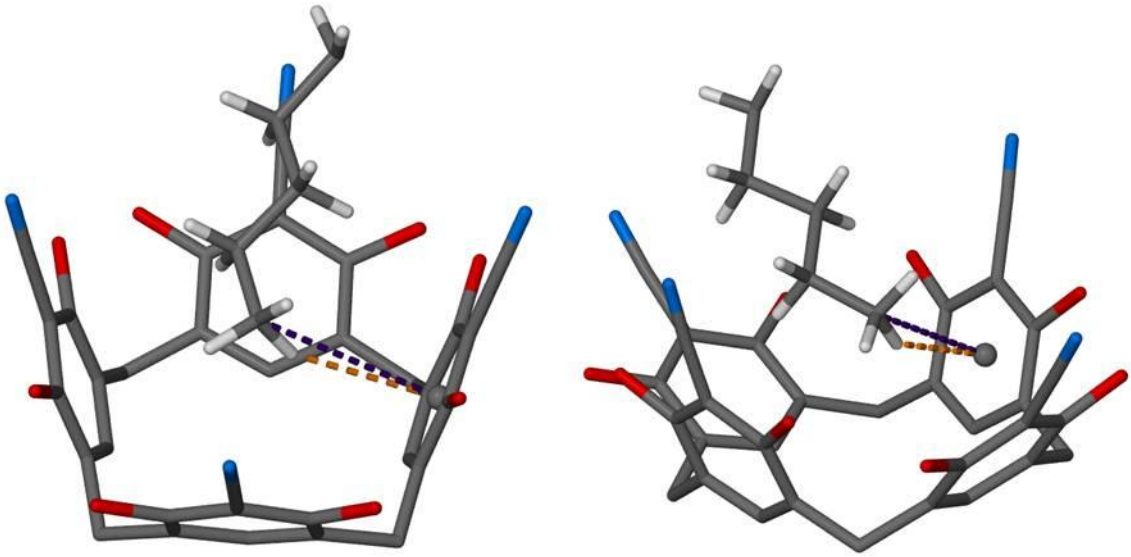

Figure 4: Two generalized views displaying CH-π interactions in cmpds 1 and 2. π Centroid shown in grey. H-π distances shown in orange, C-π distance shown in violet.

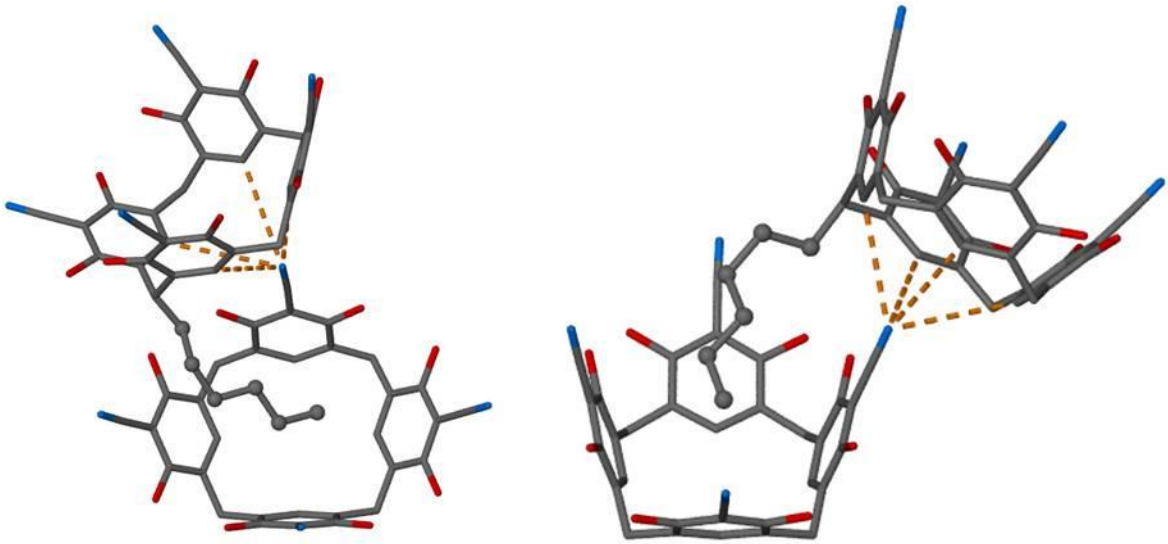

Figure 5: Two perspective views of noncovalent bonding motif described in text.

Table of Noncovalent Interaction distances for structures 1 and 2

Structure 1

		H-N distance	C-N distance	CH-N angle
CH(sp3)-N1	c29	2.56	3.51	161.39
	c35	2.57	3.55	175.07
	c41	2.93	3.91	173.34
	c47	2.99	3.97	172.79
CH(sp2)-N1	c1	2.84	3.7	151.73
	c8	2.73	3.65	164.3
	c14	2.95	3.8	149.7
	c22	2.94	3.89	177.75

	aryl ring containing	H-π	C-π	CH-π centroid angle
CH(sp3)-π	c1	2.81	3.7	150.41
(C52)	c8	4.5	4.96	112.83
	c14	3.15	3.77	122.5
	c22	3.22	3.72	113.3

Structure 2

		H-N distance	C-N distance	CH-N angle
CH(sp3)-N3	c29	2.71	3.68	167.6
	c35	2.57	3.56	178
	c41	2.78	3.77	173.9
	c47	2.72	3.71	172.4
CH(sp2)-N3	c1	2.73	3.63	159
	c8	2.64	3.59	178.6
	c15	2.72	3.63	160.9
	c22	2.76	3.71	177.7

	aryl ring containing	H-π	C-π	CH-π centroid angle
CH(sp3)-π	c1	2.88	3.62	132.7
(C40)	c8	3.19	4.03	144.4
	c14	2.93	3.77	145.3
	c22	3.51	4.18	127.1

Electronic Supplementary Material (ESI) for CrystEngComm