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N-Alkyl Ammonium Resorcinarene Polyiodides

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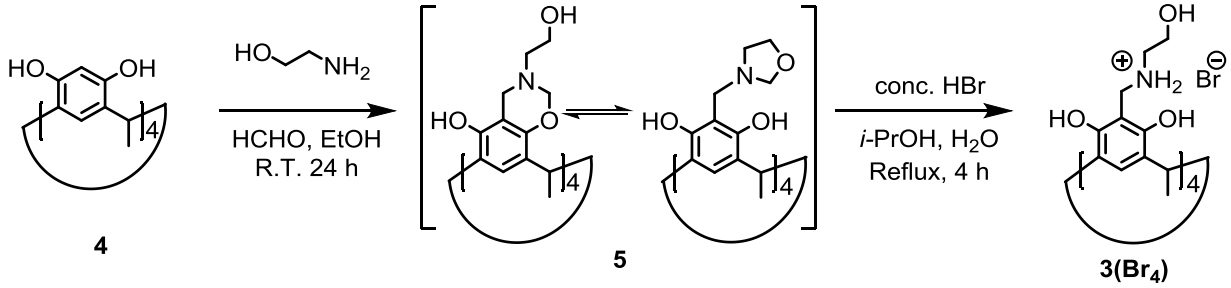
Supporting Information

I GENERAL INFORMATION

The C_1-resorcinarene **4** and the *N*-ethanol ammonium resorcinarene halides **3**(Br_4) were synthesized according to reported procedures.[1,2]. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer. All signals are given as δ values in ppm using residual solvent signals as the internal standard. Coupling constants are given in Hz. Melting points were determined with a Mettler Toledo FP62 capillary melting point apparatus. Experimental details for the synthesis and characterization data of *N*-ethanol ammonium resorcinarene bromide **3**(Br_4).

II SYNTHESIS

Synthetic details of *N*-ethanol ammonium resorcinarene bromide 3(Br_4).



Scheme S1. Synthesis of *N*-ethanol ammonium resorcinarene bromide **3**(Br_4).

a) To a solution of C_1-resorcinarene (4g, 7.344 mmols) and excess formaldehyde (8 mL) in EtOH (60 mL), 2-aminoethanol (1.86 mL, 30.8 mmols) in EtOH (15 ml) was added slowly and stirred at room temperature for 24 h. The mixture of tetrabenzoxazenes **5** was not isolated. b) Into a solution of the crude tetrabenzoxazine **5** (1.0 g, 1.129 mmol), 3 ml conc. HBr and 4 ml H_2O in 40 ml isopropanol was heated under reflux. Water and formaldehyde were removed by azeotropic distillation with chloroform. The remaining isopropanol was evaporated and the crude product triturated with diethyl ether.

N-Ethanol ammonium resorcinarene bromide **3**(Br_4) (1.01 g, 77 %). m.p. > 300 °C; ESI-TOF-MS (Positive ion mode, sprayed from MeOH): m/z = Found 837.4271 $[M\text{-}4Br\text{-}3H]^+$, 1 mDa, 1.2 ppm); calc. 837.4281. ^1H NMR (400 MHz, 298K in CD_3OD) δ: 1.85 (d, J=7.16 Hz, 12H, CH_3), 3.17 (t, 5.22 Hz, 8H, OCH_2), 3.90 (t, 5.20 Hz, 8H,NCH_2), 4.42 (s, 8H,Ar-CH_2-N), 4.72 (q, J=7.07 Hz, 4H, CH), 7.47 (s, 4H, Ar-H) ppm; ^{13}C NMR: (100 MHz, 298K in CD_3OD) δ = 18.9, 29.3, 41.2, 48.4, 56.2, 108.4, 125.4, 127.2, 150.2.

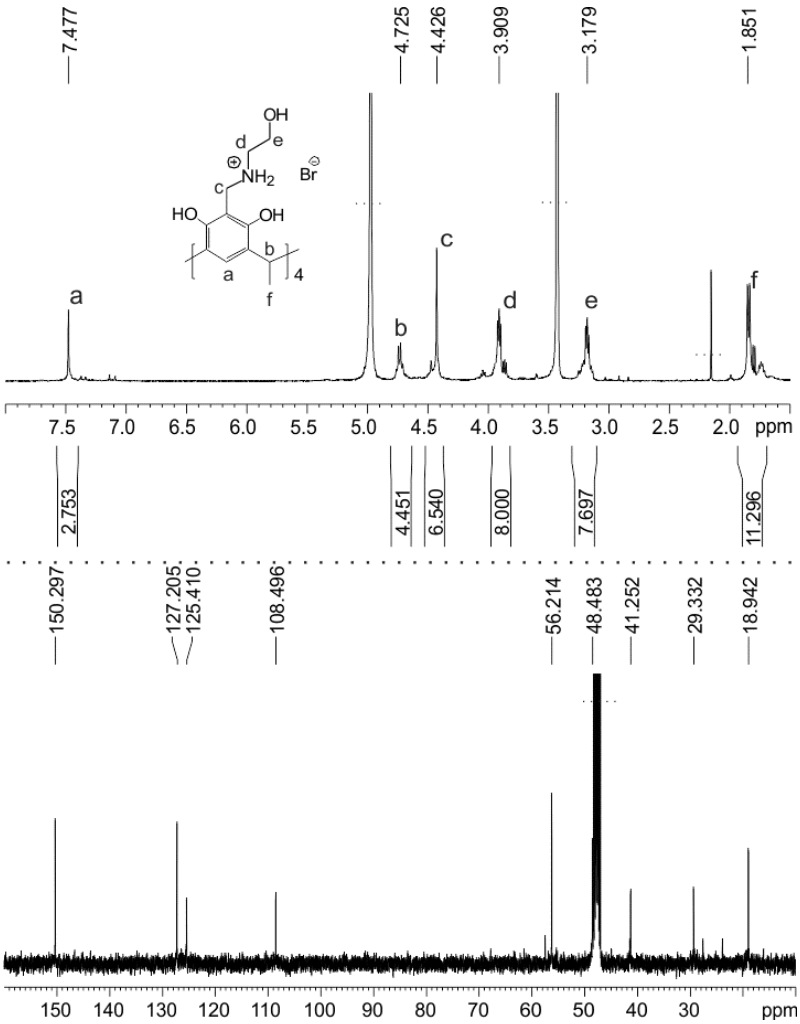


Figure S1. ^{1}H and ^{13}C NMR spectra of *N*-ethanol ammonium resorcinarene bromide **3**(Br_4).

III SOLID STATE ANALYSES

Crystals of the assembly **1**(Cl_3•I_3), **1**(Br_3•I_3), [**2**(Br_3•I_3)]$_2$ and [**3**($Br_{3.5}$)]$_2$•I_5 were obtained by slow evaporation of methanolic solution containing 1:2 mixture of the corresponding *N*-alkyl ammonium resorcinarene halide and I_2 in the presence of few drops of 1,4-dioxane. All the four data were collected at 123 K with an Agilent Super-Nova diffractometer using mirror-monochromatized Cu-*K*α (λ=1.54184Å) radiation. *CrysAlisPro*[3] was used for both data collection and processing. The intensities were corrected for absorption using gaussian integration method[3] for **1**(Cl_3•I_3) and [**3**($Br_{3.5}$)]$_2$•I_5, multi-scan[4] for **1**(Br_3•I_3), and analytical face index absorption correction method[5] for [**2**(Br_3•I_3)]$_2$. The structures were solved by Direct method with *SHELXS*[6] and refined by full-matrix least-squares methods using the *OLEX2*,[7] which utilizes the *SHELXL-2013* module.[6] All non-hydrogen atoms in the four structures were refined with anisotropic thermal parameters. In **1**(Cl_3•I_3), one of the four cyclohexane groups was slightly disordered, however without split, just geometrically restrained with "SADI" commands. The solvent water molecule was highly disordered, which was treated with split over three

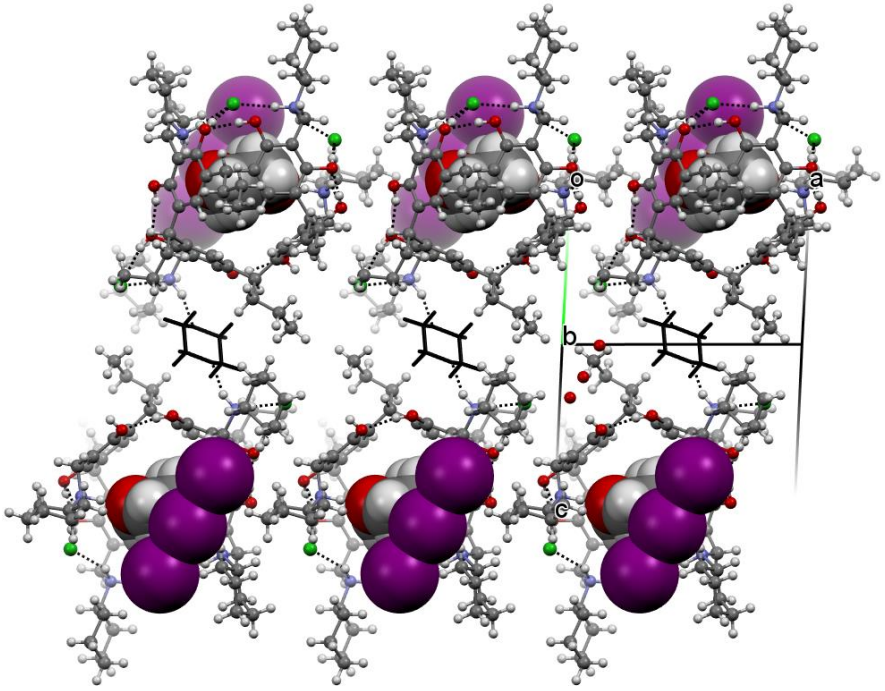
positions with fix occupancies. In [**3**($Br_{3.5}$)]$_2$•I_5, each bromide anion was disordered and split over two sites with fixed occupancies. The sum of the occupancy was 0.875 for each Br^-, thus there were 7 Br^- in total rendering the dimeric capsule of [**3**($Br_{3.5}$)]$_2$ exhibiting one positive charge, which was balanced by a pentaiodide anion. Because of the disorder or the charge polarization of I atoms, large electron peaks were observed beside the assigned I atoms. Due to the high symmetry, the guest molecule in the cavity was heavily disordered. The electron density was squeezed out by PLATON[8].

Crystal data **1**(Cl_3•I_3)**:** 0.031×0.057×0.118 mm, $C_7H_{116}N_4O_{12}Cl_3I_3$, M = 1740.75, triclinic, space group P-1, a = 12.0439(8) Å, b = 13.1940(5) Å, c = 25.6543(10) Å, α = 102.364(3)°, β = 93.086(5)°, γ = 90.337(4)°, V = 3975.7(3) Å^3, Z = 2, ρ = 1.454 g cm^{-3}, μ = 10.659 mm^{-1}, F(000) = 1788, 27119 reflections (θ_{max} = 66.750°) measured (14100 unique, R_{int} = 0.0757, completeness = 99.9%), Final R indices ($I > 2\sigma(I)$): R_1= 0.0909, wR_2 = 0.2347, R indices (all data): R_1= 0.1396, wR_2 = 0.2850. GOF = 1.030 for 895 parameters and 47 restraints, largest diff. peak and hole 1.679/–2.318 eÅ^{-3}. CCDC-1481996 contains the supplementary data for this structure.

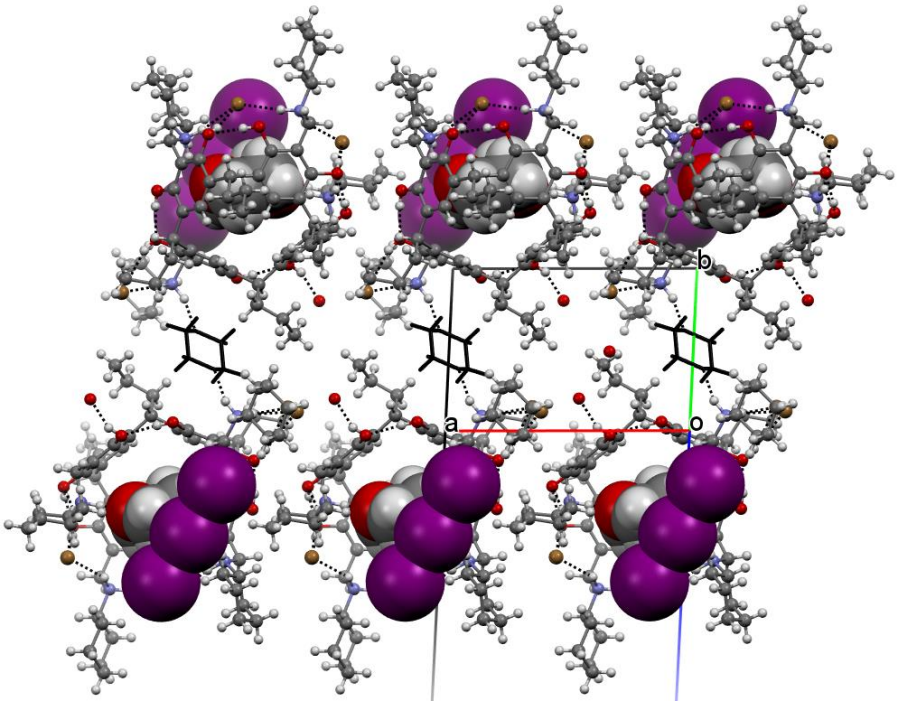
Crystal data **1**(Br_3•I_3)**:** 0.0943×0.1791×0.3704 mm, $C_{74}H_{119}N_4O_{13}Br_3I_3$, M = 18890, triclinic, space group P-1, a = 12.2171(3) Å, b = 13.1621(3) Å, c = 25.6541(6) Å, α = 77.8171(19)°, β = 86.247(2)°, γ = 89.7322(18)°, V = 4023.52(17) Å^3, Z = 2, ρ = 1.560 g cm^{-3}, μ = 11.374 mm^{-1}, F(000) = 1914, 28250 reflections (θ_{max} = 66.747°) measured (14287 unique, R_{int} = 0.0451, completeness = 99.99%), Final R indices ($I > 2\sigma(I)$): R_1= 0.0831, wR_2 = 0.2289, R indices (all data): R_1= 0.0946, wR_2 = 0.2472. GOF = 1.035 for 894 parameters and 8 restraints, largest diff. peak and hole 3.046/–1.679 eÅ^{-3}. CCDC-1481997 contains the supplementary data for this structure.

Crystal data **2**(Br_3•I_3)**:** 0.0331×0.0342×0.1561 mm, $C_{58}H_{96}N_4O_{10}Br_3I_3$, M = 1629.81, monoclinic, space group $P21/n$, a = 15.0087(4) Å, b = 27.3833(5) Å, c = 16.3215(4) Å, α = 90°, β = 91.343(2)°, γ = 90°, V = 6706.1(3) Å^3, Z = 4, ρ = 1.614 g cm^{-3}, μ = 13.511 mm^{-1}, F(000) = 3264, 29031 reflections (θ_{max} = 66.748°) measured (11813 unique, R_{int} = 0.0767, completeness = 99.3%), Final R indices ($I > 2\sigma(I)$): R_1= 0.0692, wR_2 = 0.1935, R indices (all data): R_1= 0.0994, wR_2 = 0.2275. GOF = 1.021 for 722 parameters and 23 restraints, largest diff. peak and hole 2.691/–1.564 eÅ^{-3}. CCDC-1481998 contains the supplementary data for this structure.

Crystal data [**3**($Br_{3.5}$)]$_2$•I_5**:** 0.0421×0.1285×0.2824 mm, $C_{88}H_{128}N_8O_{24}Br_7I_5$, M = 2875.85, tetragonal, space group $P4/nnc$, a = 12.3974(2) Å, b = 12.3868(2) Å, c = 36.9639(11) Å, α = 90°, β = 90°, γ = 90°, V = 5663.1(3) Å^3, Z = 2, ρ = 1.687 g cm^{-3}, μ = 14.224 mm^{-1}, F(000) = 2828, 16009 reflections (θ_{max} = 66.730°) measured (2522 unique, R_{int} = 0.0593, completeness = 99.9%), Final R indices ($I > 2\sigma(I)$): R_1= 0.1135, wR_2 = 0.3201, R indices (all data): R_1= 0.1237, wR_2 = 0.3311. GOF = 1.170 for 165 parameters and 0 restraints, largest diff. peak and hole 2.044/–4.022 eÅ^{-3}. CCDC-1481999 contains the supplementary data for this structure.

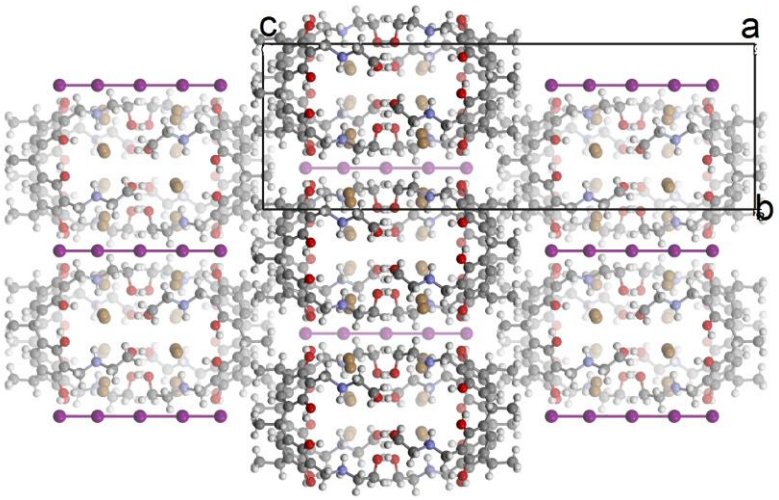


(A)

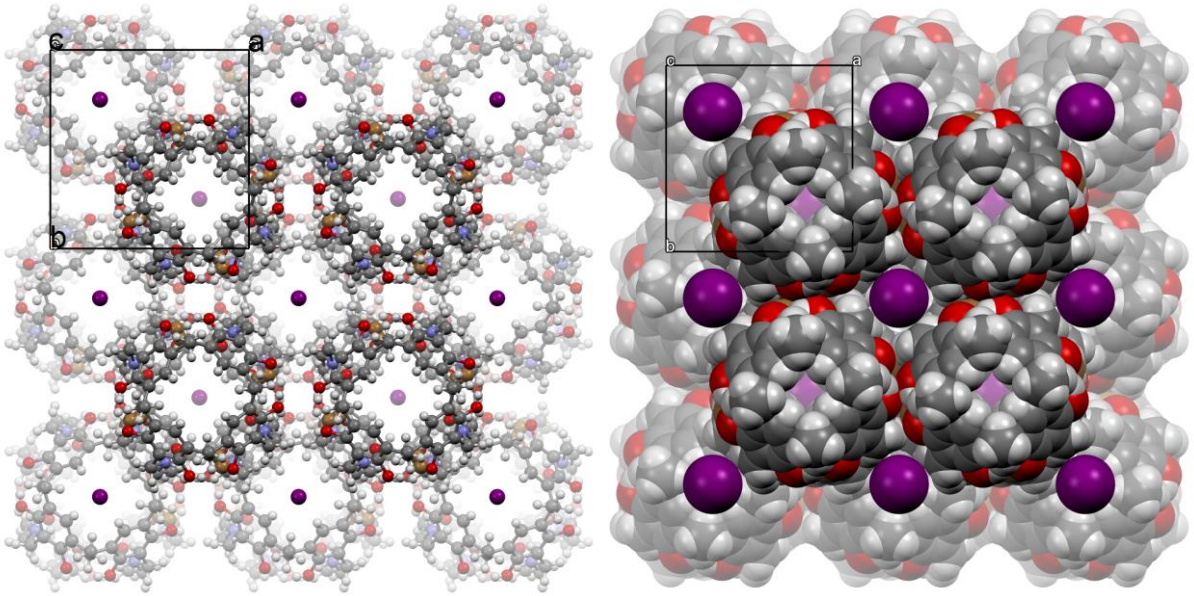


(B)

Figure S2. Packing of the assembly **1**(Cl_3•I_3) (A) and **1**(Br_3•I_3) (B) along *a* direction.



(A)



(B) (C)

Figure S3. Packing of the assembly [**3**($Br_{3.5}$)]$_2$•I_5 along *bc* plane (A), and *ac* plane in brick-and-ball model (B) and CPK model (C).

VI REFERENCES

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4. SCALE3 ABSPACK in CrysAlis PRO.

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