Dimeric Resorcinarene Salt Capsules with Very Tight Encapsulation of Anions and Guest Molecules

Fangfang Pan, Ngong Kodiah Beyeh and Kari Rissanen**

Department of Chemistry, NanoScience Center, University of Jyvaskyla , P.O. Box 35, 40014
Jyvaskyla, Finland. Fax: +358 14 260 2651; Tel: +358 14 260 2672
e-mail: kari.t.rissanen@jyu.fi, ngong.k.beyeh@jyu.fi

Supporting Information

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I General Information

All materials were commercial and used as such unless otherwise mentioned. The *N*-cyclohexyl ammonium resorcinarene salt **4**(OTf)$_4$ was synthesized according to reported procedures.[1,2]. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) and Bruker Avance DRX 500 (500 MHz for ^{1}H and 126 MHz for ^{13}C) spectrometers. 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. The mass spectrometric measurements were done on micromass LCT ESI-TOF instrument.

II Syntheses

N- Cyclohexyl ammonium resorcinarene triflate 4(OTf)$_4$:

A solution of the *N*-cyclohexyl tetrabenzoxaxine (1.0 g, 0.964 mmol), conc. trifluoromethanesulfonic acid (3 ml) and H_2O (4 ml) in isopropanol (40 ml) was heated under reflux for four hours. Water and formaldehyde were removed by azeotropic distillation with chloroform. The remaining isopropanol was removed by evaporation and the crude product dissolved in CH_2Cl_2. The remaining acid was then removed by extraction with water. The solvent was removed and the product triturated with diethyl ether, filtered and dried in vacuum (1.37 g 89 %). Mp > 213 ^oC. [$C_{64}H_{88}N_4O_{20}F_{12}S_4$, MW 1589.63 g/mol; HRMS (ESI): m/z calcd for $C_{60}H_{86}N_4O_8$: 495.3217 [**4**-2H]$^{2+}$; found: 495.3231, 2.8 ppm]; ^{1}H NMR (400 MHz, DMSO-d$_6$, 300 K) δ: 9.09 (br, 8H, Ar-OH), 8.08 (br, 8H, NH_2), 7.56 (s, 4H, Ph-H), 4.54 (q, J 6.8 Hz 4H, CH), 4.00 (br, 8H, Ar-CH_2-N), 2.94 (m, 4H, N-CH), 2.03-1.06 (m, 52H, CH_2, CH_3); ^{13}C NMR (100 MHz, 300 K, DMSO-d$_6$) δ: 150.7, 126.9, 108.7, 57.4, 55.6, 28.9, 25.9, 25.1, 24.4, 20.6.

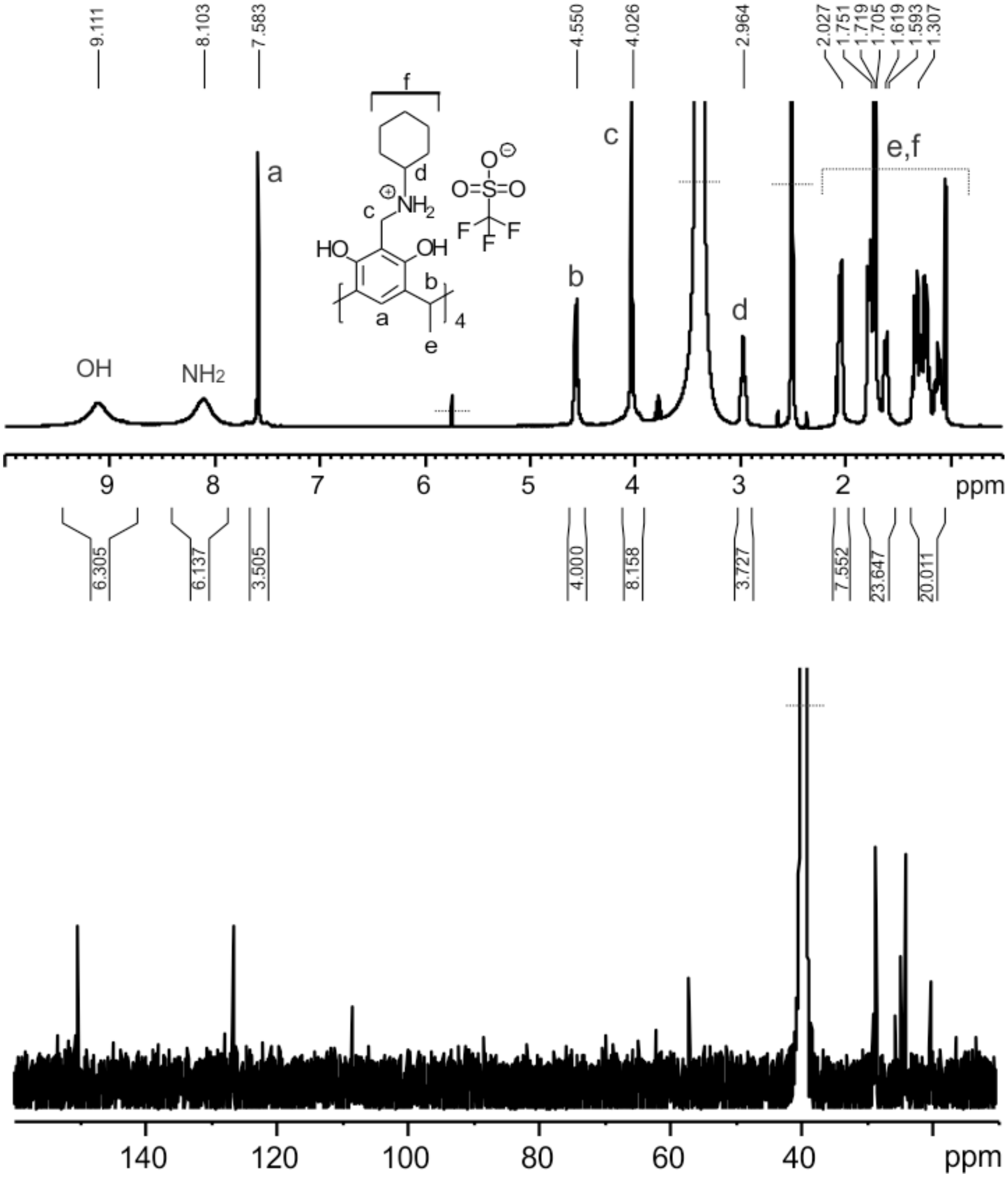

Figure S1. ^{1}H and ^{13}C NMR of **4**(OTf)$_4$.

III X-Ray Crystallography:

Single crystal X-ray data for (2×1,4-dioxane•2×H_2O)$_2$@(**4**(OTf)$_4$)$_2$ were collected at 173(2) K using an Agilent Super-Nova diffractometer with a mirror-monochromatized Mo-*K*α (λ = 0.71073 Å) radiation, while data collection for (OTf•MeOH)$_2$@(**4**(OTf)$_3$MeOH)$_2$ was performed at 123(2) K with Agilent Super-Nova dual wavelength diffractometer with a micro-focus X-ray source and multilayer optics monochromatized Cu-*K*α (λ = 1.54184 Å) radiation. Program *CrysAlisPro*[3] was used for the data collection and reduction. The intensities were corrected for absorption using analytical face index absorption correction method[4] for (2×1,4-dioxane•2×H_2O)$_2$@(**4**(OTf)$_4$)$_2$, and gaussian face index absorption correction method[3] for (OTf•MeOH)$_2$@(**4**(OTf)$_3$MeOH)$_2$. The structures were solved with direct methods (*SHELXS*[5]) and refined by full-matrix least squares on F^2 using the *OLEX2*[6], which utilizes the *SHELXL*-2013 module[5]. Anisotropic displacement parameters were assigned to non-H atoms. All the hydrogen atoms were refined using riding models with U_{eq}(H) of 1.5U_{eq}(parent) for hydroxyl and terminal methyl groups, and 1.2 U_{eq}(parent) for other groups. One of the four triflates and one of the four cyclohexyl groups in (2×1,4-dioxane•2×H_2O)$_2$@(**4**(OTf)$_4$)$_2$, and two of the triflates and two of the cyclohexyl groups in (OTf•MeOH)$_2$@(**4**(OTf)$_3$MeOH)$_2$, were found to be disordered. They were split over two positions according to the difference Fourier maps. Anisotropic displacement parameters and geometry of the disordered groups were constrained or restrained if necessary. Crystal of (OTf•MeOH)$_2$@(**4**(OTf)$_3$MeOH)$_2$ is twinning. The hklf5 format reflections file with two components was generated by PLATON[7]. The final refined BASF factor was 0.399.

Crystal data:

(OTf•MeOH)$_2$@(4(OTf)$_3$MeOH)$_2$: 0.08×0.26×0.37 mm, $C_{60}H_{88}N_4O_8 \cdot 4(CF_3O_3S)$ 2(CH_4O), M = 1653.70, monoclinic, space group $P2_1/n$, a = 15.4805(7) Å, b = 31.8766(7) Å, c = 15.9510(5) Å, α = 90°, β = 104.209(4)°, γ = 90°, V = 7630.5(5) Å^3, Z = 4, ρ = 1.440 g cm^{-3}, μ = 2.057 mm^{-1}, $F(000)$ = 3472, 49353 reflections (θ_{max} = 76.74°) measured (13487 unique, R_{int} = 0.043, completeness = 99.8%), Final R indices ($I > 2\sigma(I)$): R_1= 0.0891, wR_2 = 0.2802, R indices (all data): R_1= 0.0991, wR_2 = 0.2872. GOF = 1.097 for 1168 parameters and 79 restraints, largest diff. peak and hole 0.776/–0.664 eÅ^{-3}. CCDC-xxxxxx contains the supplementary data for this structure.

(2×1,4-dioxane•2×H_2O)$_2$@(4(OTf)$_4$)$_2$: 0.09×0.25×0.37 mm, $C_{60}H_{88}N_4O_8 \cdot 4(CF_3O_3S)$ 2($C_4H_8O_2$) 2(H_2O), M = 1801.86, triclinic, space group P-1, a = 16.3576(14) Å, b = 17.0042(13) Å, c =

18.5089(13) Å, α = 69.135(7)°, β = 67.660(7)°, γ = 67.136(8)°, V = 4254.4(7) $Å^3$, Z = 2, ρ = 1.407 g cm^{-3}, μ = 0.215 mm^{-1}, $F(000)$ = 1896, 39947 reflections (θ_{max} = 25.250°) measured (15415 unique, R_{int} = 0.0501, completeness = 99.9%), Final R indices ($I > 2\sigma(I)$): R_1= 0.0670, wR_2 = 0.1636, R indices (all data): R_1= 0.1169, wR_2 = 0.1988. GOF = 1.032 for 1197 parameters and 60 restraints, largest diff. peak and hole 0.554/–0.365 $eÅ^{-3}$. CCDC-xxxxx contains the supplementary data for this structure.

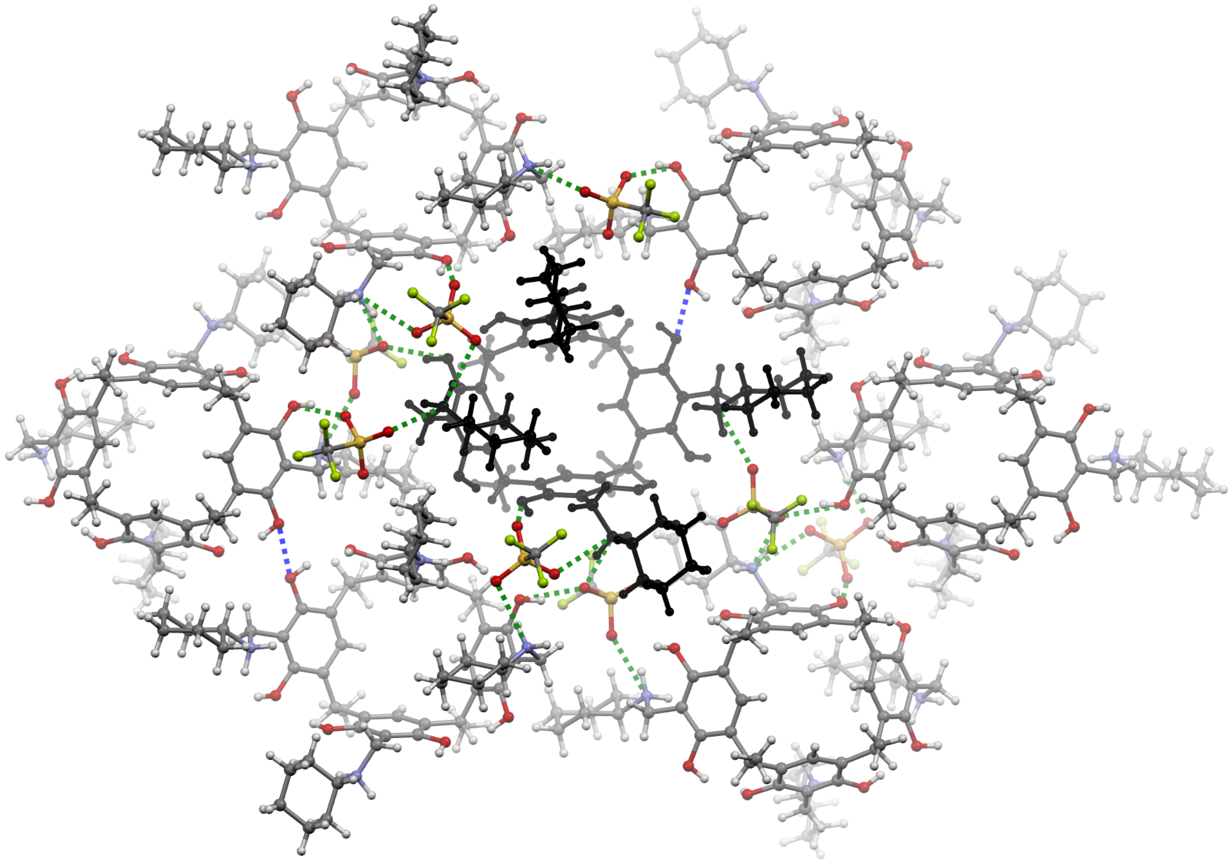

Figure S3. Intermolecular bridging effect of triflates in the assembly of $(OTf•MeOH)_2@(\mathbf{4}(OTf)_3MeOH)_2$ with the relevant resorcinarene cation in black. The blue dotted lines highlight the OH···O interactions directly between two resorcinarene frames. The bound guests are omitted for clarity.

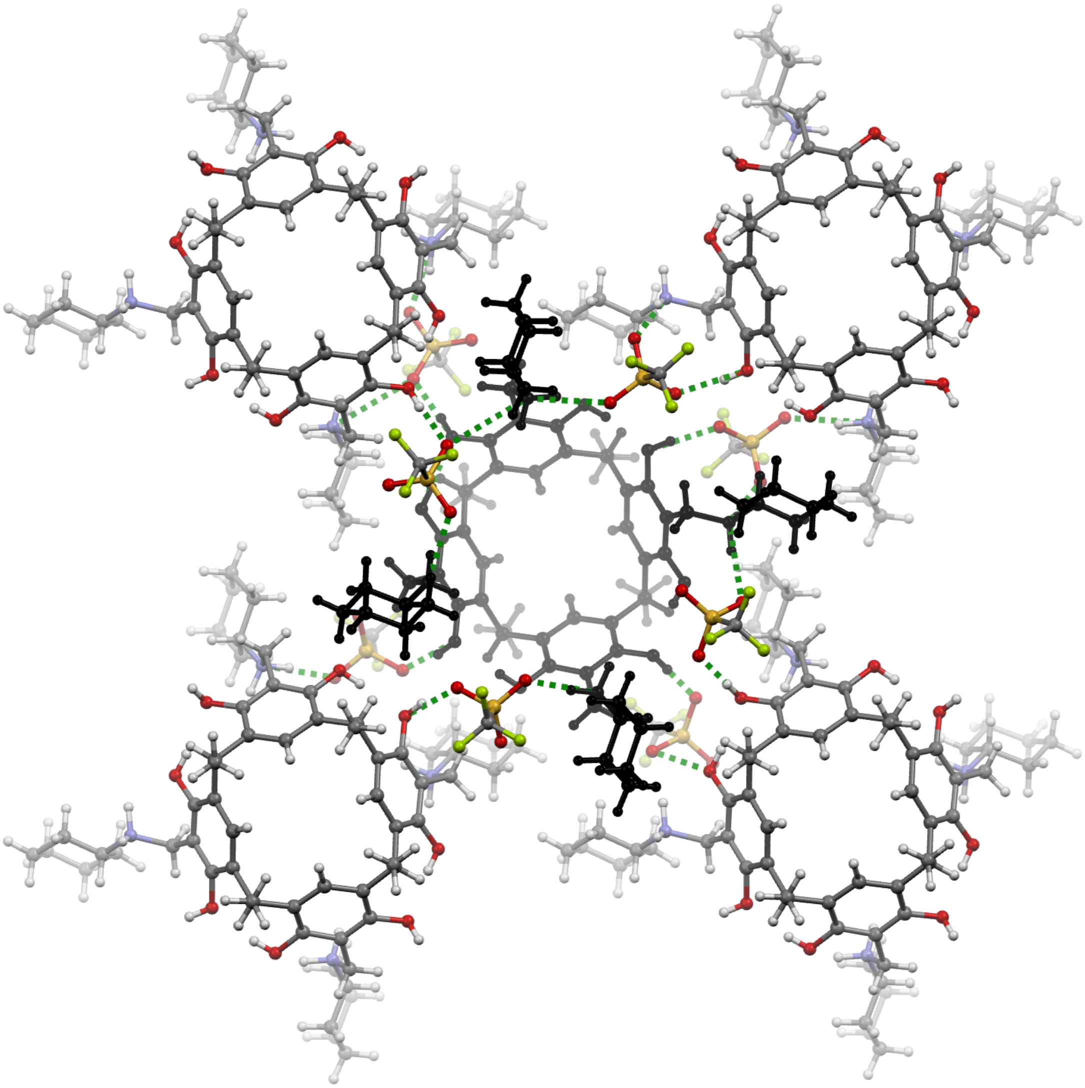

Figure S4. Intermolecular bridging effect of triflates in the assembly of $(2\times1,4\text{-dioxane}\bullet2\times H_2O)_2@(\mathbf{4}(OTf)_4)_2$ with the relevant resorcinarene cation in black. The bound guests are omitted for clarity.

IV References:

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