

# Deprotonation of Resorcinarenes by Mono- and Diamine Bases: Complexation and Intermolecular Interactions in the Solid State

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## Supplementary Information

As the first step the determination of the deprotonation was done by locating the H-atoms from the  $\Delta F$  map and then refining them from their located positions as riding atoms. Then the geometry of the intra- and intermolecular H-bonds were evaluated as the deprotonated OH group, viz. phenolate oxygen, shows a distinct and strong 3-fold H-bond acceptor behavior in a tetrahedral configuration with much shorter intermolecular (C-O-...O-C or -O-... N-C) distances (2.52 – 2.67 Å for I and II with only exception, 2.76 Å, of C-O-...O-CH<sub>3</sub> in structure I) as for the non-deprotonated, normal resorcinarene OH groups. Based on  $\Delta F$  H-atom positions and interaction geometry two OH groups in structure I and one OH in structure II were assigned to be deprotonated.

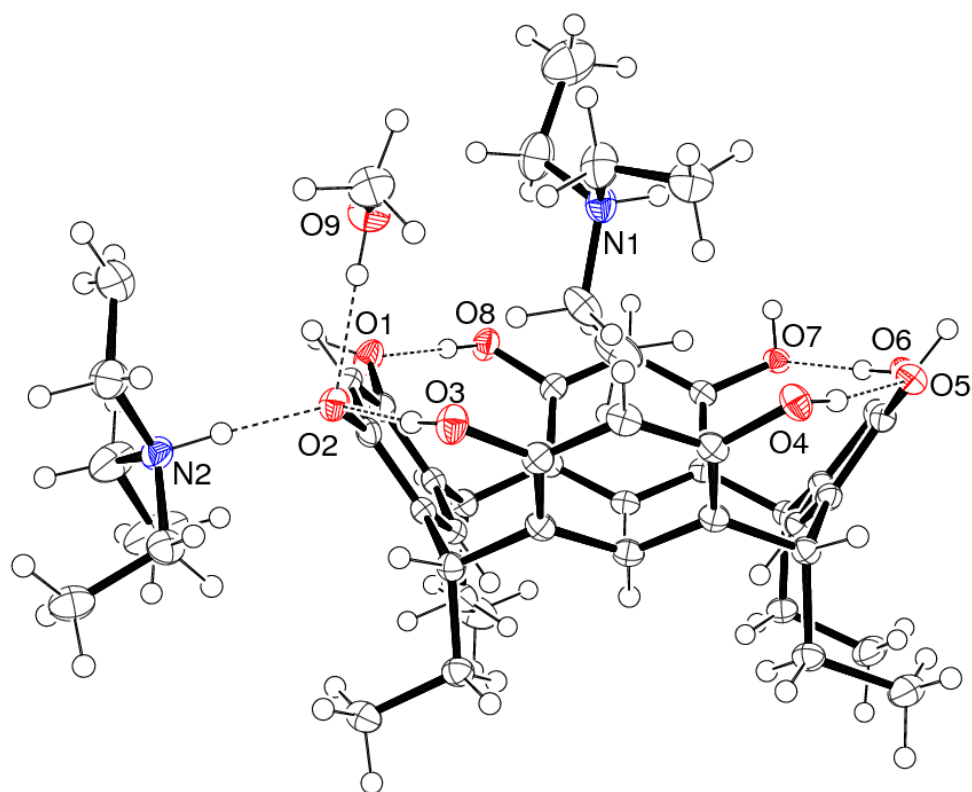


Figure S1. Thermal ellipsoid (50 % probability) diagram of structure **I** showing atom labelling for N and O atoms and hydrogen bonds inside AU. The disorder in cation A inside the bowl is removed for clarity.

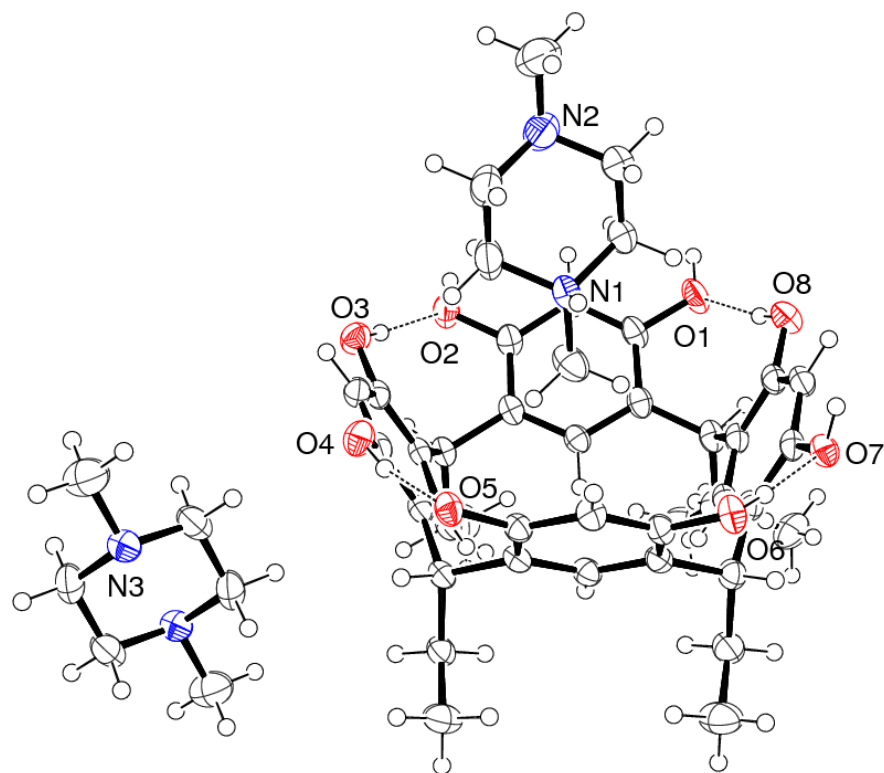


Figure S2. Thermal ellipsoid (50 % probability) diagram of structure **II** showing atom labelling for N and O atoms inside AU and intramolecular hydrogen bonds.

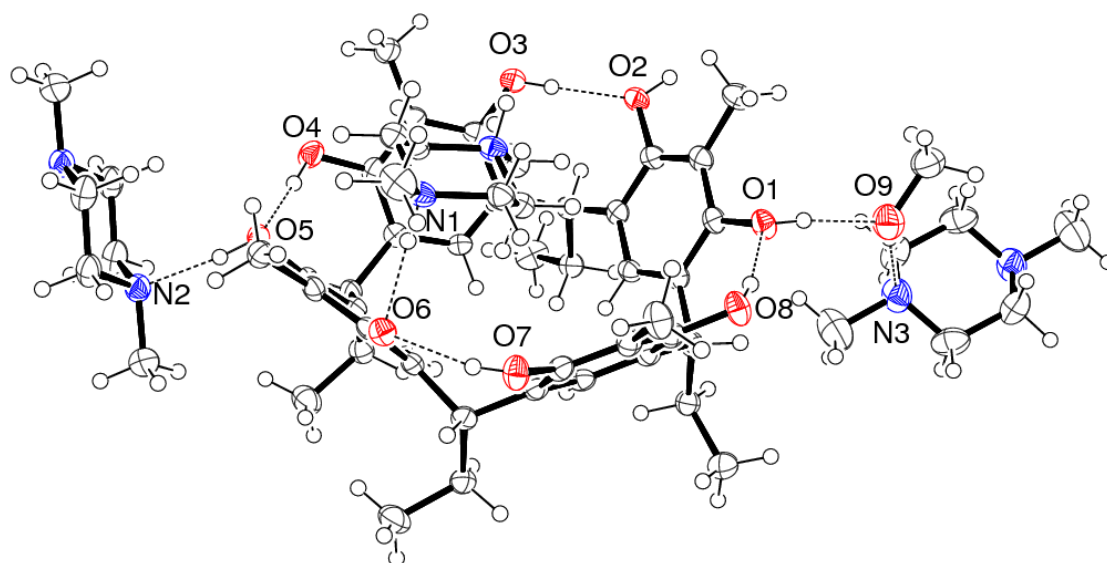


Figure S3. Thermal ellipsoid (50 % probability) diagram of structure **III** showing atom labelling for N and O atoms and hydrogen bonds inside AU.

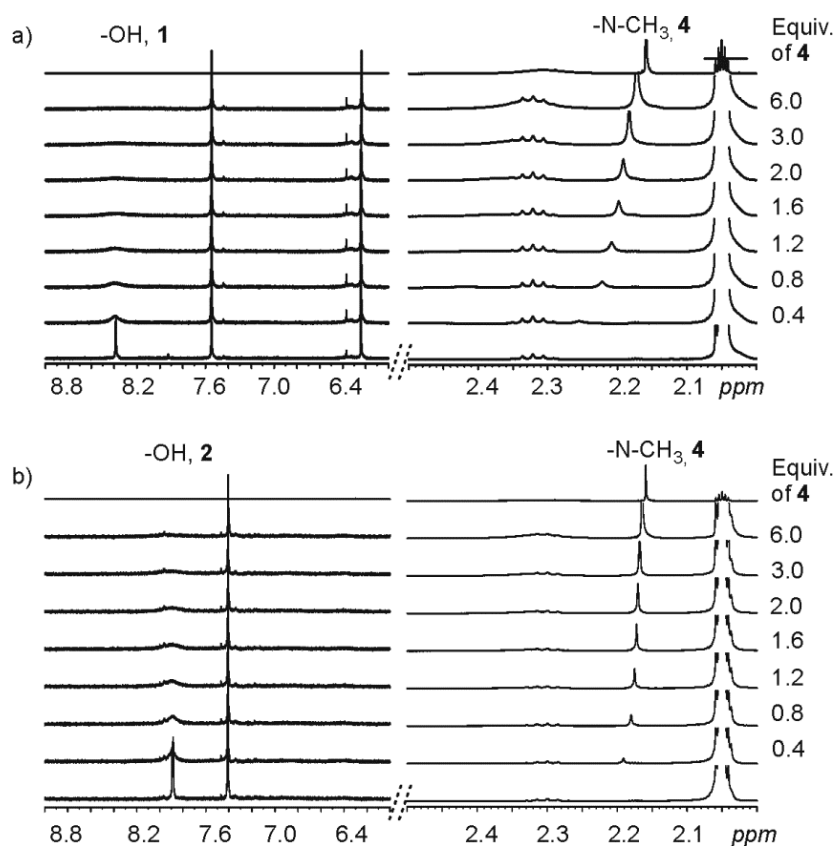


Figure S4. <sup>1</sup>H NMR spectral changes observed upon the addition of diamine **4** to resorcinarene **1** (a) and resorcinarene **2** (b) in acetone-*d*<sub>6</sub> at 303 K

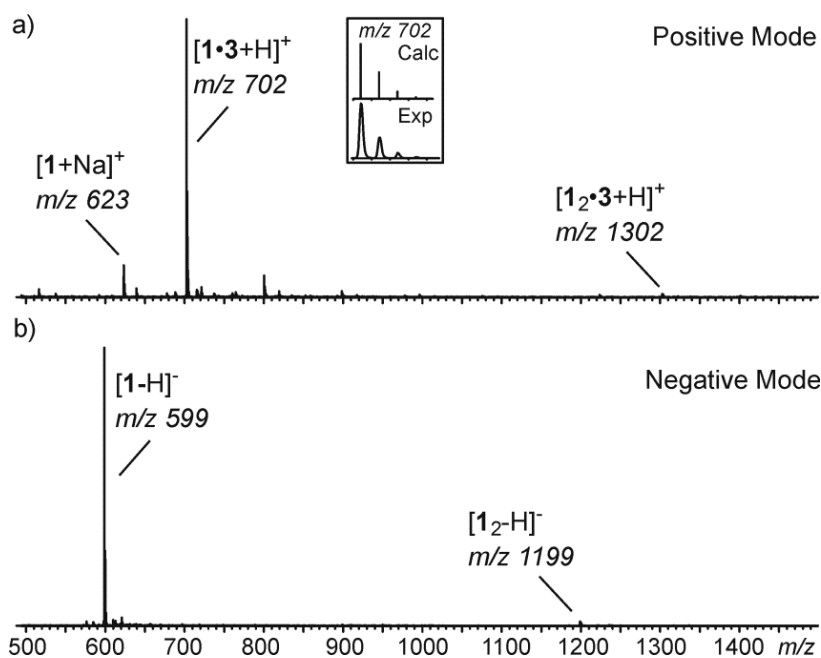


Figure S5. Electrospray ionization mass spectra of a mixture of resorcinarene **1** and monoamine **3**. (a) Positive ion mode showing the 1:1 monomeric  $[1\cdot3+H]^+$   $m/z$  702 and dimeric  $[1_2\cdot3+H]^+$   $m/z$  1302 complexes. (b) Negative ion mode showing the deprotonated resorcinarene monomer  $[1-H]^-$   $m/z$  599 and dimer  $[1_2-H]^-$   $m/z$  1199.

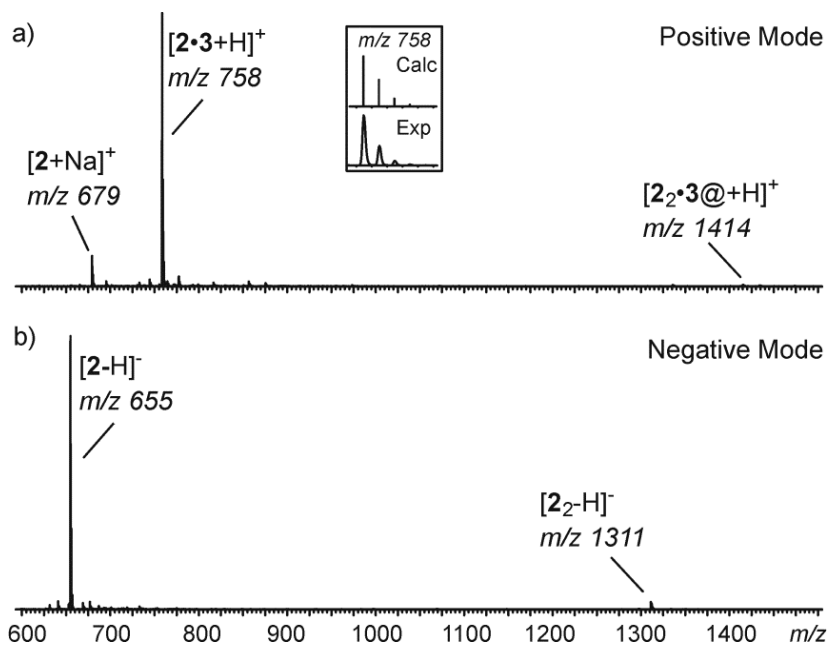


Figure S6. Electrospray ionization mass spectra of a mixture of resorcinarene **2** and monoamine **3**. (a) Positive ion mode showing the 1:1 monomeric  $[2\cdot3+H]^+$   $m/z$  758 and dimeric  $[2_2\cdot3+H]^+$   $m/z$  1414 complexes. (b) Negative ion mode showing the deprotonated resorcinarene monomer  $[2-H]^-$   $m/z$  655 and dimer  $[2_2-H]^-$   $m/z$  1311.

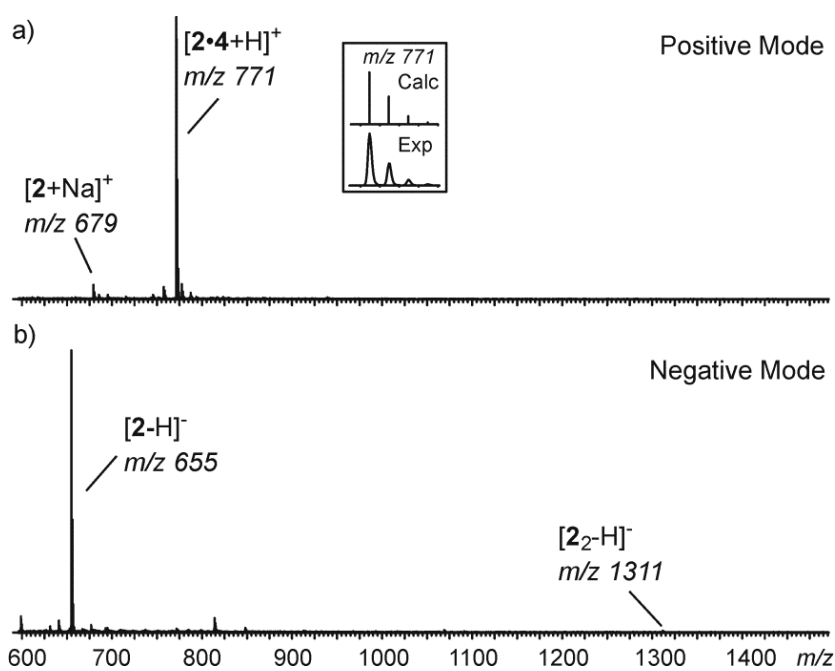


Figure S7. Electrospray ionization spectra of a mixture of resorcinarene **2** and monoamine **4**. (a) Positive ion mode showing the 1:1 monomeric  $[2\cdot 4+H]^+$   $m/z$  771 complex. (b) Negative ion mode showing the deprotonated resorcinarene monomer  $[2-H]^-$   $m/z$  655 and dimer  $[2_2-H]^-$   $m/z$  1311.