Supplementary Information

As the first step the determination of the deprotonation was done by locating the H-atoms from the ΔF 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-CH3 in structure I) as for the non-deprotonated, normal resorcinarene OH groups. Based on ΔF 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. $^1$H NMR spectral changes observed upon the addition of diamine 4 to resorcinarene 1 (a) and resorcinarene 2 (b) in acetone-$d_6$ 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•3+H]+ m/z 702 and dimeric [12•3+H]+ m/z 1302 complexes. (b) Negative ion mode showing the deprotonated resorcinarene monomer [1-H]− m/z 599 and dimer [12-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•3+H]+ m/z 758 and dimeric [22•3+H]+ m/z 1414 complexes. (b) Negative ion mode showing the deprotonated resorcinarene monomer [2-H]− m/z 655 and dimer [22-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•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.