Experimental Section.

$^1$H NMR (600 MHz) and $^{13}$C NMR (151 MHz) spectra were recorded on a Brüker DRX-600 spectrometer. Unless otherwise indicated, all proton spectra were obtained at 300 K and all 2D spectra were obtained at 303 K. 2D NOESY spectra were acquired with a delay time (d1) of 1.0 s and mixing times (d8) of 0.3–0.4 s. The rates of chemical exchange were measured using Exchange Spectroscopy (EXSY) by integrating the peaks of the 2D NOESY using XWINNMR followed by processing with D2DNMR software.

C$_{11}$-footed resorcin[4]arene 1 was prepared using literature methods.

The volumes of van der Waals surfaces of the guests were calculated using WabLabViewer Pro (Molecular Simulation Inc., version 5, 2000).

Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA). Chloroform-$d$ and benzene-$d_6$ samples were saturated with water and filtered before use. All other reagents were purchased from Aldrich (St. Louis, MO) or Acros Organics and used without further purification.

Figure S1. Variable temperature $^1$H NMR of resorcinarene 1 (12 mM) + cis-1,2-cyclohexanediol (3). From bottom to top: 300 K, 310 K, 320 K, and 330 K. Only downfield (resorcinarene host) and upfield (encapsulated diol) portions are shown. Under these conditions at room temperature, the resorcinarene exists in two forms—assembled and unassembled—in slow exchange. The associated and unassociated peaks coalesce between 320 and 330 K.

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Figure S2. $^1$H NMR of 1 (12 mM) with L-phenylalanine (4) and L-phenylalanine methyl ester hydrochloride with and without CD$_3$OD.

Figure S3. $^1$H NMR of 1 (12 mM) after sonication with solid $p$-methylphenylalanine (top), cyclohexylalanine (middle), and leucine (bottom).
Figure S4. $^1$H NMR of 1 (12 mM) with 12 mM total salt concentration. Et$_3$NHCl (top), Pr$_2$EtNHCl (middle), and 1:1 mixture of each (bottom). Only the upfield region is shown. The spectrum of each sample sharpens with heating, with some additional melting of the assembly.

Figure S5. Resorcinarene (1) + tetrapentylammonium bromide (top) and tetraethylammonium bromide (bottom). For each spectrum, [(C$_{5}$H$_{11}$)$_{4}$NBr] + [Et$_{4}$NBr] = 9 mM.
Figure S6. Resorcinarene + Et₄NBr (top), Et₄NBF₄ (bottom), and a mixture of both (middle). Only the upfield region is shown. The spectrum of Et₄NCl (not shown) is very similar to that of Et₄NBF₄. Tetraethylammonium tosylate cause significant melting of the capsule, and we have not yet found other useful, proton-containing counterions for NMR analysis.
**Figure S7.** Dynamic 1D NOESY spectrum. In each spectrum, the methine proton at 4.3 ppm is irradiated. The NOE intensity of the aryl proton at 7.2 ppm is given as a function of mixing time with and without guest.

**Figure S8.** 2D NOESY spectrum of 1 (12 mM) and cis-1,2-cyclohexanediol (3) (24 mM) in CDCl₃ at 50°C. Chemical exchange between 3 inside (red) and outside (black) was confirmed by a separate 2D ROESY experiment. For the complex between resorcinarene and diol 3, excess guest caused the appearance of a new set of host peaks—monomeric resorcinarene in slow exchange with the hexamer. The host peaks coalesce upon heating to about 50°C. Some broadening was also observed for the protons of the bound guest.