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Binding of alkyl halides in water-soluble cavitands with urea rims

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Instrumentation. ¹H NMR spectra were obtained at 600 MHz on a Bruker DRX-600 spectrometer equipped with a 5 mm DCH cryoprobe. Spectra were recorded at 298 K unless otherwise stated. Chemical shifts are expressed in parts per million (δ scale) with respect to tetramethylsilane and are referenced to the proton signal of residual, non-deuterated solvent [D₂O: δ 4.79 for ¹H NMR;] for ¹H NMR.

Materials. All reagents and solvents were purchased from commercial suppliers.

A general statement. The orientations of the tumbling guests were calculated from the percent of the maximum $\Delta\delta$ that the observed CH₃ signals represent. For example, the CH₃ of the 1-chlorohexane appears at $\Delta\delta = -3.9$ ppm (binding with cavitand 2) which represents 80 % of the maximum $\Delta\delta$ of -4.8 ppm (CH₃ is down and at the bottom of cavitand 2) with 20% of $\Delta\delta$ of -0.4 ppm (CH₃ is up and near the rim).



Figure S1. ¹H NMR spectra (600MHz, D₂O, 298K) of cavitand **2** (1.0 mM) + 1-chloropentane (0.5 mM), cavitand **2** (1.0 mM) + 1-bromopentane (0.5 mM), cavitand **2** (1.0 mM) + 1-iodopentane (0.5 mM).



Figure S2. ¹H NMR spectra (600MHz, D₂O, 298K) of cavitand **3** (1.0 mM) + 1-chloropentane (0.5 mM), cavitand **3** (1.0 mM) + 1-bromopentane (0.5 mM), cavitand **3** (1.0 mM) + 1-iodopentane (0.5 mM).



Figure S3. ¹H NMR spectra (600MHz, D₂O, 298K) of cavitand **2** (1.0 mM) + 1-chlorohexane (0.5 mM), cavitand **2** (1.0 mM) + 1-bromohexane (0.5 mM), cavitand **2** (1.0 mM) + 1-iodohexane (0.5 mM).



Figure S4. ¹H NMR spectra (600MHz, D₂O, 298K) of cavitand **3** (1.0 mM) + 1-chlorohexane (0.5 mM), cavitand **3** (1.0 mM) + 1-bromohexane (0.5 mM), cavitand **3** (1.0 mM) + 1-iodohexane (0.5 mM).



Figure S5. ¹H NMR spectra (600MHz, D₂O, 298K) of cavitand **2** (1.0 mM) + 1-chlorononane (0.5 mM) (2:1), cavitand **2** (1.0 mM) + 1-bromononane (0.5 mM) (2:1), cavitand **2** (1.0 mM) + 1-iodononane (0.5 mM) (2:1).



Figure S6. ¹H NMR spectra (600MHz, D₂O, 298K) of cavitand **3** (1.0 mM) + 1-chlorononane (0.5 mM), cavitand **3** (1.0 mM) + 1-bromononane (0.5 mM), cavitand **3** (1.0 mM) + 1-iodononane (0.5 mM).



Figure S7. ¹H NMR spectra (600MHz, D₂O, 298K) of cavitand **2** (1.0 mM) + 1-chlorohexane (1.0 mM) (1:1), cavitand **2** (1.0 mM) + 1-bromohexane (1.0 mM) (1:1), cavitand **2** (1.0 mM) + 1-chlorohexane (1.0 mM) (1:1).



Figure S8. ¹H NMR spectra (600MHz, D₂O, 298K) of cavitand **2** (1.0 mM) + 1-bromohexane (1.0 mM) (1:1), cavitand **2** (1.0 mM) + 1-iodohexane (1.0 mM) (1:1), cavitand **2** (1.0 mM) + 1-bromohexane (1.0 mM) (1:1).



Figure S9. ¹H NMR spectra (600MHz, D₂O, 298K) of cavitand **2** (1.0 mM) + 1-chlorohexane (1.0 mM) (1:1), cavitand **2** (1.0 mM) + 1-iodohexane (1.0 mM) (1:1), cavitand **2** (1.0 mM) + 1-chlorohexane (1.0 mM) + 1-iodohexane (1.0 mM) (1:1).



Figure S10. ¹H NMR spectra (600MHz, D_2O , 298K) of cavitand 2 (1.0 mM) + 1-chlorononane (0.5 mM) (2:1).