**Electronic Supplementary Information** 

## Selective molecular recognition of methylated lysines and arginines by cucurbit[6]uril and cucurbit[7]uril in aqueous solution

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**Figure S1.** <sup>1</sup>H NMR titration of LysMe<sub>3</sub> (1.0 mmol dm<sup>-1</sup>) by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C). (a) 0.0, (b) 0.22, (c) 0.46, (d) 0.71, (e) 1.09, (f) 1.11, (g) 1.20, (h) 1.56, and (i) 2.04 eq CB[7].

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**Figure S2.** <sup>1</sup>H NMR titration of LysMe<sub>2</sub> (1.0 mmol dm<sup>-1</sup>) by CB[7] (impurity signals \*) in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C). (a) 0.0, (b) 0.15, (c) 0.30, (d) 0.49, (e) 0.65, (f) 0.78, (g) 0.96, (h) 1.22, (i) 1.54, and (j) 3.52 eq CB[7].

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**Figure S3.** <sup>1</sup>H NMR titration of LysMe (0.50 mmol dm<sup>-1</sup>) by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25  $^{\circ}$ C). (a) 0.00, (b) 0.23, (c) 0.42, (d) 0.68, (e) 0.78, (f) 1.38, (g) 1.81, (h) 2.36, (i) 2.85, (j) 3.27, (k) 4.08, and (l) 4.31 eq CB[7].



**Figure S4.** <sup>1</sup>H NMR titration of Lys (1.0 mmol dm<sup>-1</sup>) by CB[7] (impurity signal \*) in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C). (a) 0.0, (b) 0.17, (c) 0.40, (d) 0.60, (e) 0.80, (f) 1.00, and (g) 1.20 eq CB[7].



**Figure S5.** Plot of  $\Delta \delta_{obs}$  (H<sub> $\epsilon$ </sub> proton) against [CB[7]] for the titration of LysMe with CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C). Solid line represents fit to  $K_{CB[7]}$  = 1.8 x 10<sup>3</sup> dm<sup>3</sup> mol<sup>-1</sup>.



**Figure S6.** <sup>1</sup>H NMR titration of Lys (1.0 mmol dm<sup>-1</sup>) by CB[7] (impurity signal \*) in D<sub>2</sub>O (0.10 mol dm<sup>-3</sup> DCl, 50 mmol dm<sup>-3</sup> NaCl, pD = 2.0, 25 °C). (a) 0.0, (b) 0.17, (c) 0.40, (d) 0.60, (e) 0.80, (f) 1.00, and (g) 1.20 eq CB[7].



**Figure S7.** <sup>1</sup>H NMR titration of LysMe<sub>3</sub> (1.0 mmol dm<sup>-1</sup>) by CB[7] in D<sub>2</sub>O (10 mmol dm<sup>-3</sup> DCl, 50 mmol dm<sup>-3</sup> NaCl buffer, pD = 2.0, 25 °C). (a) 0.0, (b) 0.22, (c) 0.46, (d) 0.71, (e) 1.09, (f) 1.11, (g) 1.20, and (h) 1.56 eq CB[7].



**Figure S8.** <sup>1</sup>H NMR titration of Lys (0.5 mmol dm<sup>-1</sup>) by CB[6] in D<sub>2</sub>O (0.10 mol dm<sup>-3</sup> NaCl, 25 °C). (a) 0.0, (b) 0.22, (c) 0.46, (d) 0.71, and (e) 1.09 eq CB[6].



**Figure S9.** Plot of  $\Delta \delta_{obs}$  against [CB[6]] for the H $\epsilon$  proton for the binding of lysine (0.30 mmol dm<sup>-3</sup>) by CB[6] in D<sub>2</sub>O (100 mmol dm<sup>-3</sup> NaCl).





**Figure S10.** <sup>1</sup>H NMR titration of LysMe (0.5 mmol dm<sup>-1</sup>) by CB[6] in D<sub>2</sub>O (0.10 mol dm<sup>-3</sup> NaCl, 25 °C). (a) 0.0, (b) 0.47, (c) 0.90, (d) 1.34, (e) 2.14, (f) 2.43, (g) 3.14, (h) 4.30, (i) 4.58, and (j) 5.98 eq CB[6].

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**Figure S11.** <sup>1</sup>H NMR titration of LysMe<sub>2</sub> (0.5 mmol dm<sup>-1</sup>) by CB[6] in D<sub>2</sub>O (0.10 mol dm<sup>-3</sup> NaCl, 25  $^{\circ}$ C). (a) 0.0, (b) 0.54, (c) 1.00, (d) 1.64, (e) 2.06, (f) 4.07, (g) 5.12, and (h) 9.06 eq CB[6].

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**Figure S12.** <sup>1</sup>H NMR titration of LysMe<sub>3</sub> (0.5 mmol dm<sup>-1</sup>) by CB[6] in D<sub>2</sub>O (0.10 mol dm<sup>-3</sup> NaCl, 25  $^{\circ}$ C). (a) 0.0, (b) 0.22, (c) 0.46, (d) 0.71, (e) 1.09, (f) 1.11, (g) 1.20, (h) 2.4, (i) 3.48, (j) 4.14, (k) 5.40, (l) 6.16, and (m) 6.95 eq CB[6].



**Figure S13.** <sup>1</sup>H NMR titration of Lys (0.5 mmol dm<sup>-1</sup>) by CB[6] at pD = 1.0 in D<sub>2</sub>O (0.10 mol dm<sup>-3</sup> DCl and 0.10 mol dm<sup>-3</sup> NaCl, 25 °C). (a) 0.0, (b) 0.21, (c) 0.44, (d) 0.68, (e) 1.04, (f) 1.06, (g) 1.14, and (h) 1.94 eq CB[6].



**Figure S14** <sup>1</sup>H NMR titration of LysMe (0.5 mmol dm<sup>-1</sup>) by CB[6] at pD = 1.0 in D<sub>2</sub>O (0.10 mol dm<sup>-3</sup> DCl and 0.10 mol dm<sup>-3</sup> NaCl, 25 °C). (a) 0.0, (b) 0.24, (c) 0.45, (d) 0.67, (e) 1.07, (f) 1.22, (g) 2.15, and (h) 2.90 eq CB[6].



**Figure S15** <sup>1</sup>H NMR titration of LysMe<sub>2</sub> (0.5 mmol dm<sup>-1</sup>) by CB[6] at pD = 1.0 in D<sub>2</sub>O (0.10 mol dm<sup>-3</sup> DCl and 0.10 mol dm<sup>-3</sup> NaCl, 25 °C). (a) 0.0, (b) 0.40, (c) 0.50, (d) 0.70, (e) 1.03, (f) 1.27, (g) 1.43, (h) 2.04, (i) 2.56, and (j) 4.52 eq CB[6].

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**Figure S16** <sup>1</sup>H NMR titration of LysMe<sub>3</sub> (0.30 mmol dm<sup>-1</sup>) by CB[6] at pD = 1.0 in D<sub>2</sub>O (0.10 mol dm<sup>-3</sup> DCl and 0.10 mol dm<sup>-3</sup> NaCl, 25 °C). (a) 0.0, (b) 0.40, (c) 0.75, (d) 1.10, (e) 1.60, (f) 2.15, (g) 4.95, and (h) 6.10 eq CB[6].



**Figure S17.** Benesi-Hildebrand plots of  $\Delta_{obs}^{-1}$  against [CB[6]]<sup>-1</sup> for the <sup>1</sup>H NMR titrations of (**■**) HLysMe (H<sub>Me</sub>), (**▲**) HLysMe<sub>2</sub> (H<sub> $\delta$ </sub>) and (**●**) HLysMe<sub>3</sub> (H $\epsilon$ ) with CB[6] in 0.10 M DCl (containing 0.10 M NaCl).



**Figure S18.** The structures of the protonated HLysMe<sub>n</sub> guest series. The values adjacent to the guest protons are the <sup>1</sup>H NMR chemical shift changes ( $\Delta \delta_{\text{lim}}$ , ppm) induced by cucurbit[6]uril complexation in 0.10 M DCl (containing 0.10 M NaCl). The values were determined from the chemical shift changes in Figure S13 for HLys and from extrapolations using the limiting chemical shift changes determined in Figure S17 for the methylated HLysMe<sub>n</sub> guests.



**Figure S19.** <sup>1</sup>H NMR titration of acetyllysine (1.0 mmol dm<sup>-1</sup>) by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25  $^{\circ}$ C). (a) 0.0, (b) 0.18, (c) 0.34, (d) 0.50, (e) 0.69, (f) 0.91, (g) 1.08, (h) 1.39, (i) 1.72, and (j) 4.04 eq CB[7].



**Figure S20**. Benesi-Hildebrand plot for the binding of acetyllysine by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25  $^{\circ}$ C) using Me proton resonance.





**Figure S21.** <sup>1</sup>H NMR titration of L-arginine (1.0 mmol dm<sup>-1</sup>) by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C). (a) 0.00, (b) 0.17, (c) 0.34, (d) 0.54, (e) 0.71, (f) 0.93, (g) 1.17, (h) 1.48, (i) 1.80, and (j) 4.21 eq CB[7].

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**Figure S22.** <sup>1</sup>H NMR titration of methylarginine (1.0 mmol dm<sup>-1</sup>) by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C). (a) 0.00, (b) 0.26, (c) 0.51, (d) 0.94, (e) 1.11, (f) 1.36, (g) 1.59, (h) 2.18, (i) 2.68, and (j) 5.20 eq CB[7].





**Figure S23.** <sup>1</sup>H NMR titration of asymmetric dimethylarginine (1.0 mmol dm<sup>-1</sup>) by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C). (a) 0.00, (b) 0.25, (c) 0.48, (d) 0.69, (e) 1.45, (f) 1.89, (g) 2.30, (h) 2.70, (i) 3.19, and (j) 4.34 eq CB[7].

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**Figure S24.** <sup>1</sup>H NMR titration of symmetric dimethylarginine (1.0 mmol dm<sup>-1</sup>) by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C). (a) 0.00, (b) 0.20, (c) 0.42, (d) 0.63, (e) 0.79, (f) 1.05, (g) 1.23, (h) 1.55, (i) 1.93, and (j) 5.06 eq CB[7].



**Figure S25.** Benesi-Hildebrand plot for the binding of L-arginine by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C) using H $\alpha$  proton resonance.



**Figure S26.** Benesi-Hildebrand plot for the binding of N-methylarginine by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C) using H $\alpha$  proton resonance.



**Figure S27.** Plots of  $\Delta\delta_{obs}$  (H $\delta$ ) against [CB[7]] for the binding of asymmetric dimethylarginine (1.0 mmol dm<sup>-3</sup>) by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C).



**Figure S28**. Plot of  $\Delta \delta_{obs}$  for the guest methyl proton resonance against [CB[7]] for the binding of symmetric dimethylarginine (1.0 mmol dm<sup>-3</sup>) by CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C).



**Figure S29.** Plot of  $\log K_{CB[7]}$  (LysMe<sub>n</sub>) against n in LysMe<sub>n</sub> for binding with CB[7] in D<sub>2</sub>O (50 mmol dm<sup>-3</sup> NaOAc buffer, pD = 4.7, 25 °C).