

## Supplementary Data

### Reasons for the exclusive formation of heterodimeric capsules between tetra-tolyl and tetra-tosylurea calix[4]arenes

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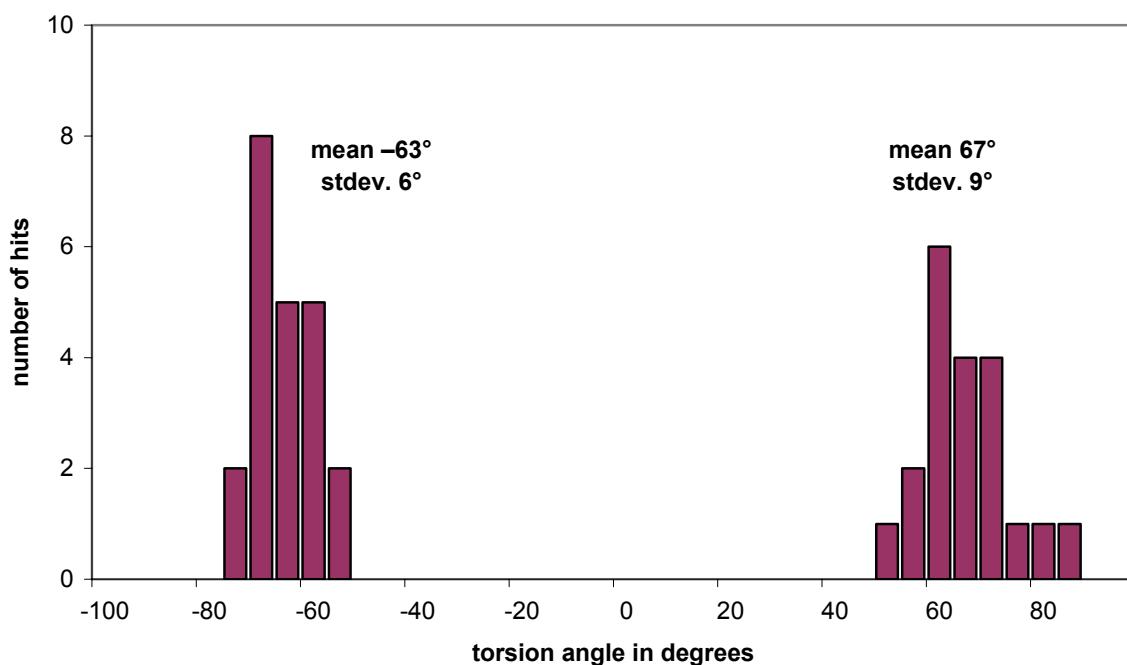
**Table S1** Average energetic and geometric parameters of the monomers **1a** and **1b**.

	<b>1a</b>	<b>1b</b>
steric energy (kcal/mol)	-404.4 ± 10.1	-531.7 ± 9.4
number of hydrogen bonds	1.5	2.6
NH <sub>α</sub> ···O distance [Å]	2.57 (0.54)	2.30 (0.28) / 2.28 (0.28)
NH <sub>β</sub> ···O distance [Å]	1.97 (0.43)	2.20 (0.27) / 2.21 (0.28)

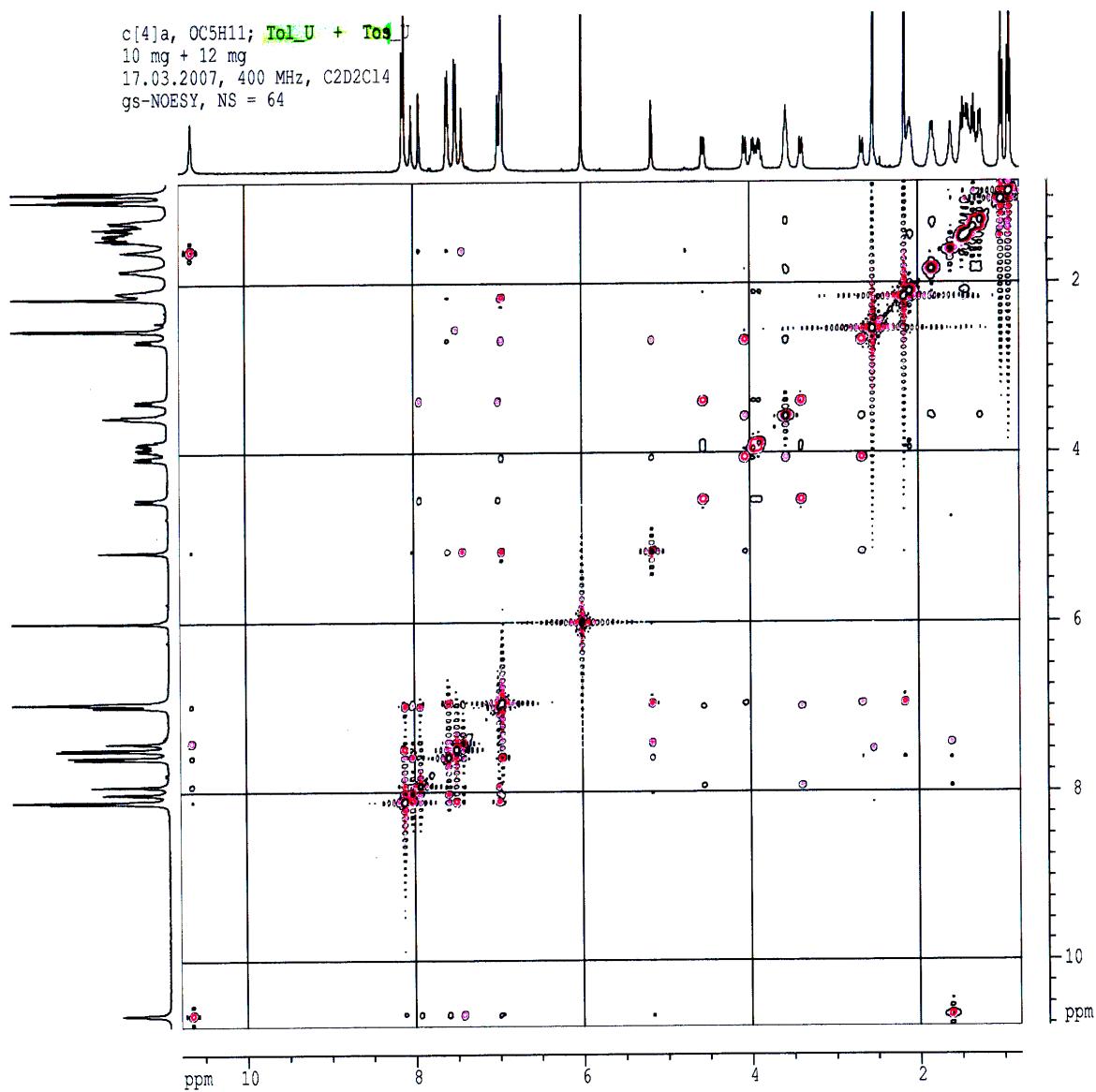
**Fig. S1** Compounds used for the calculation of RESP charges and the corresponding RESP derived charges for the constituting fragments of the tetra-tolyl- and tetra-tosylurea calix[4]arenes **1a** and **1b**. Also given are the corresponding atom types used for the AMBER 7 calculations.

Molecule for the RESP calculation	Fragment in <b>1a</b> and <b>1b</b>
	<p>ha 0.038627 ca -0.431319 hc 0.246135 OS 0.398208 ca -0.041323 hc -0.321509 hc 0.020305 c3 -0.142453</p>
	<p>H -0.000905 c3 -0.016219 hc 0.024671 H -0.004687 c3 -0.02173 hc 0.011261 H -0.046496 c3 -0.002184 hc 0.027834 H -0.123689 c3 H</p>
	<p>hc -0.184499 ca 0.060447 ha 0.155236 ca -0.213451 hn -0.224506 n 0.281157 c=O 0.814188 hn -0.631287 n 0.335841 hc -0.561498 ha 0.28988 ca 0.117426 hn -0.407674</p>
	<p>hc -0.170747 ca 0.067613 ha 0.151522 ca -0.189939 hn -0.148637 o=S(=O)(=O) 0.170187 n 0.022901 c=O 0.976926 hn -0.505173 n 0.318654 hc -0.738172 o=S(=O)(=O) 0.865329 c=O -0.512613 hn -0.369763</p>

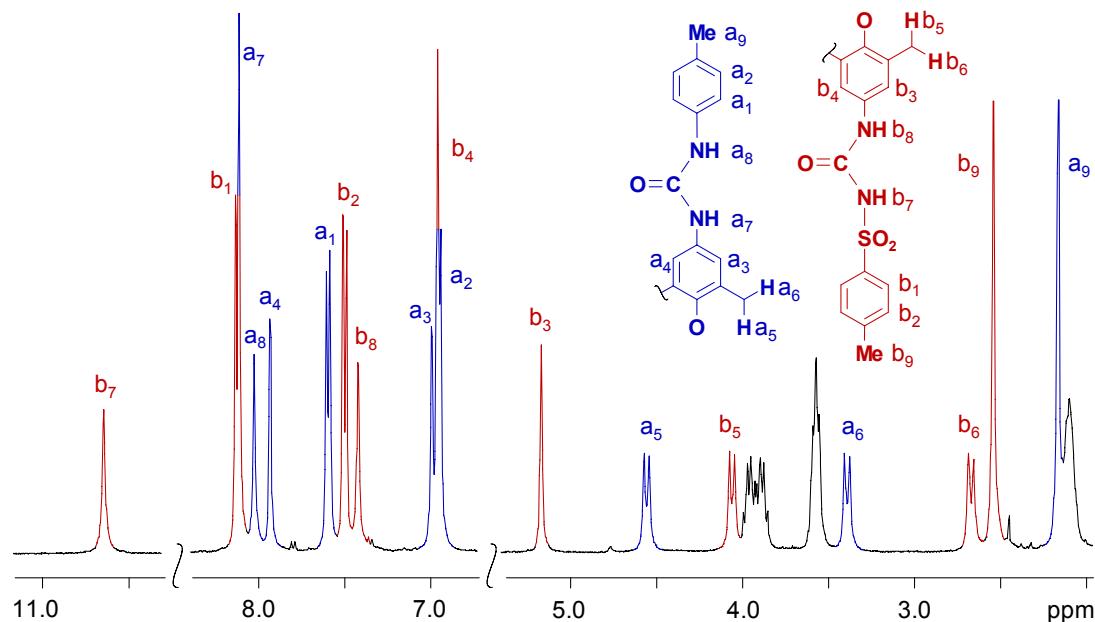
**Figure S2.** Histogram of the C–S–N–C dihedral angles of acyclic sulfonyl ureas (S–N–C(O)–N angle restricted to  $180 \pm 20^\circ$ ) in the Cambridge Structural Database (2006 release). The total number of hits was 42, multiple crystal structures were omitted from the data set.



**Fig. S3** NOESY spectrum of the heterodimer **1a**•**1b** in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> (mixing time = 300 ms).



**Table S2** Interpretation of NOESY spectrum of the heterodimer **1a·1b** in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>.



proton 1	proton 2	intens.	proton 1	proton 2	intens.	
a <sub>1</sub>	a <sub>2</sub>	++	b <sub>1</sub>	b <sub>2</sub>	++	
	a <sub>8</sub>	++		b <sub>7</sub>	+	
	a <sub>9</sub>	+		b <sub>9</sub>	+	
	b <sub>3</sub>	+	b <sub>2</sub>	b <sub>1</sub>	++	
	b <sub>6</sub>	+		b <sub>9</sub>	++	
	b <sub>7</sub>	+		b <sub>4</sub>	++	
	a <sub>2</sub>	++		b <sub>5</sub>	+	
				b <sub>6</sub>	++	
a <sub>3</sub>	a <sub>4</sub>	++		b <sub>7</sub>	+	
	a <sub>5</sub>	+		b <sub>8</sub>	++	
	a <sub>6</sub>	++		a <sub>1</sub>	+	
	a <sub>7</sub>	++		a <sub>8</sub>	+	
	b <sub>7</sub>	+	b <sub>4</sub>	b <sub>3</sub>	++	
a <sub>4</sub>	a <sub>3</sub>	++		b <sub>5</sub>	+	
	a <sub>5</sub>	+		b <sub>6</sub>	++	
	a <sub>6</sub>	++		a <sub>8</sub>	+	
	a <sub>7</sub>	+	b <sub>5</sub>	b <sub>3</sub>	+	
	b <sub>7</sub>	+		b <sub>4</sub>	+	
a <sub>5</sub>	a <sub>3</sub>	+		b <sub>6</sub>	++	
	a <sub>4</sub>	+		b <sub>3</sub>	++	
	a <sub>6</sub>	++		b <sub>4</sub>	++	
a <sub>6</sub>	a <sub>3</sub>	++	b <sub>6</sub>	b <sub>5</sub>	++	
	a <sub>4</sub>	++		b <sub>3</sub>	++	
a <sub>7</sub>	a <sub>5</sub>	++		b <sub>4</sub>	++	
	a <sub>3</sub>	++		b <sub>5</sub>	++	
	a <sub>4</sub>	+		a <sub>1</sub>	+	
	a <sub>8</sub>	++	b <sub>7</sub>	b <sub>1</sub>	+	
a <sub>8</sub>	a <sub>1</sub>	++		b <sub>3</sub>	+	
				b <sub>8</sub>	++	
				a <sub>1</sub>	+	
				a <sub>3</sub>	+	

	a <sub>7</sub>	++		a <sub>4</sub>	+
	b <sub>3</sub>	+	b <sub>8</sub>	b <sub>3</sub>	++
	b <sub>4</sub>	+	b <sub>8</sub>	b <sub>7</sub>	++
a <sub>9</sub>	a <sub>1</sub>	+	b <sub>9</sub>	b <sub>1</sub>	+
	a <sub>2</sub>	++		b <sub>2</sub>	++

**Fig. S4** Intermolecular contacts for the heterodimer **1a·1b** (derived from the NOESY spectrum).

