

## Electronic Supplementary Information for:

### Influence of H-bond Competitors on the Solvent-dependent Structures of an Octaurea-Calix[4]tube

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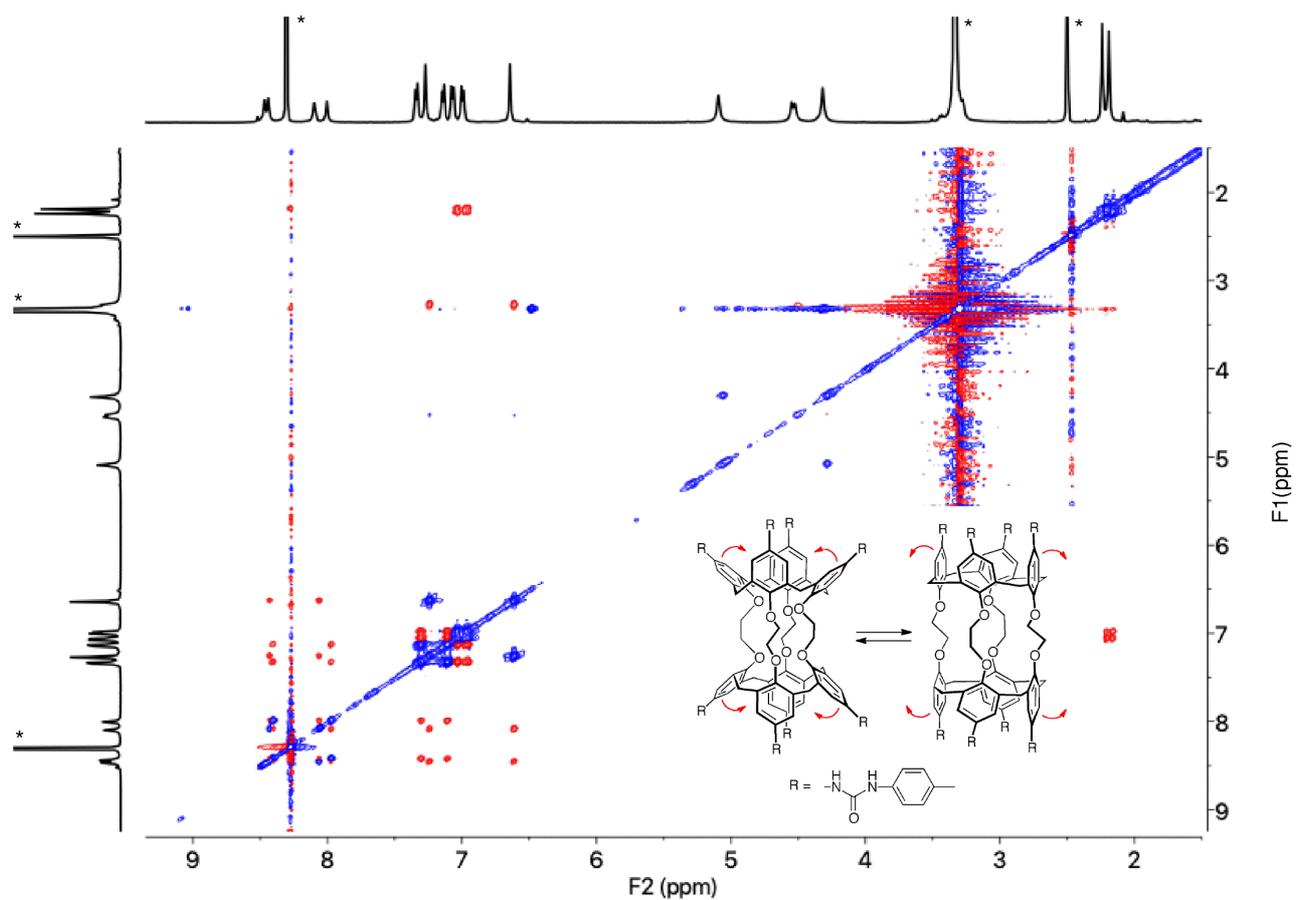
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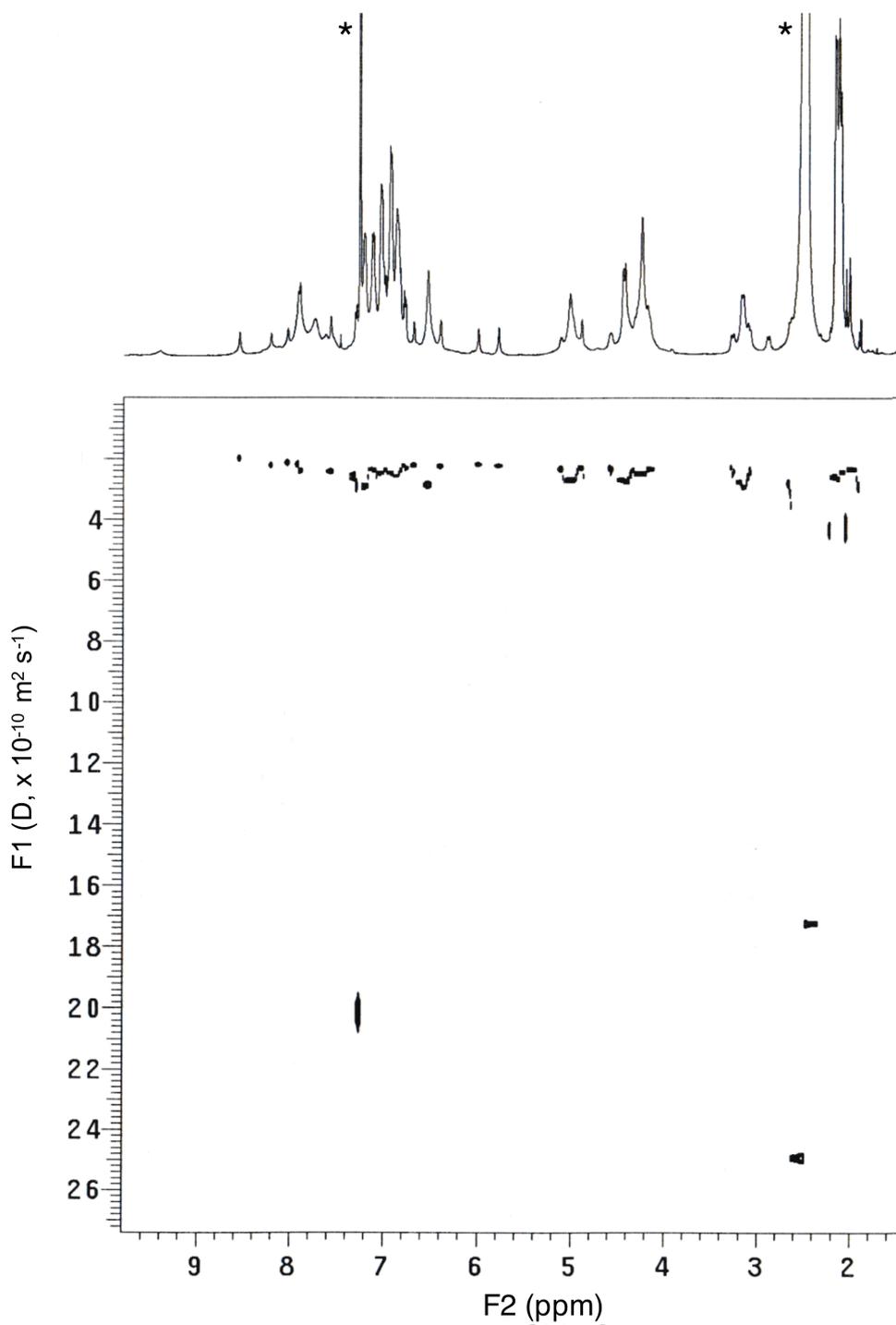
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#### Table of Contents:

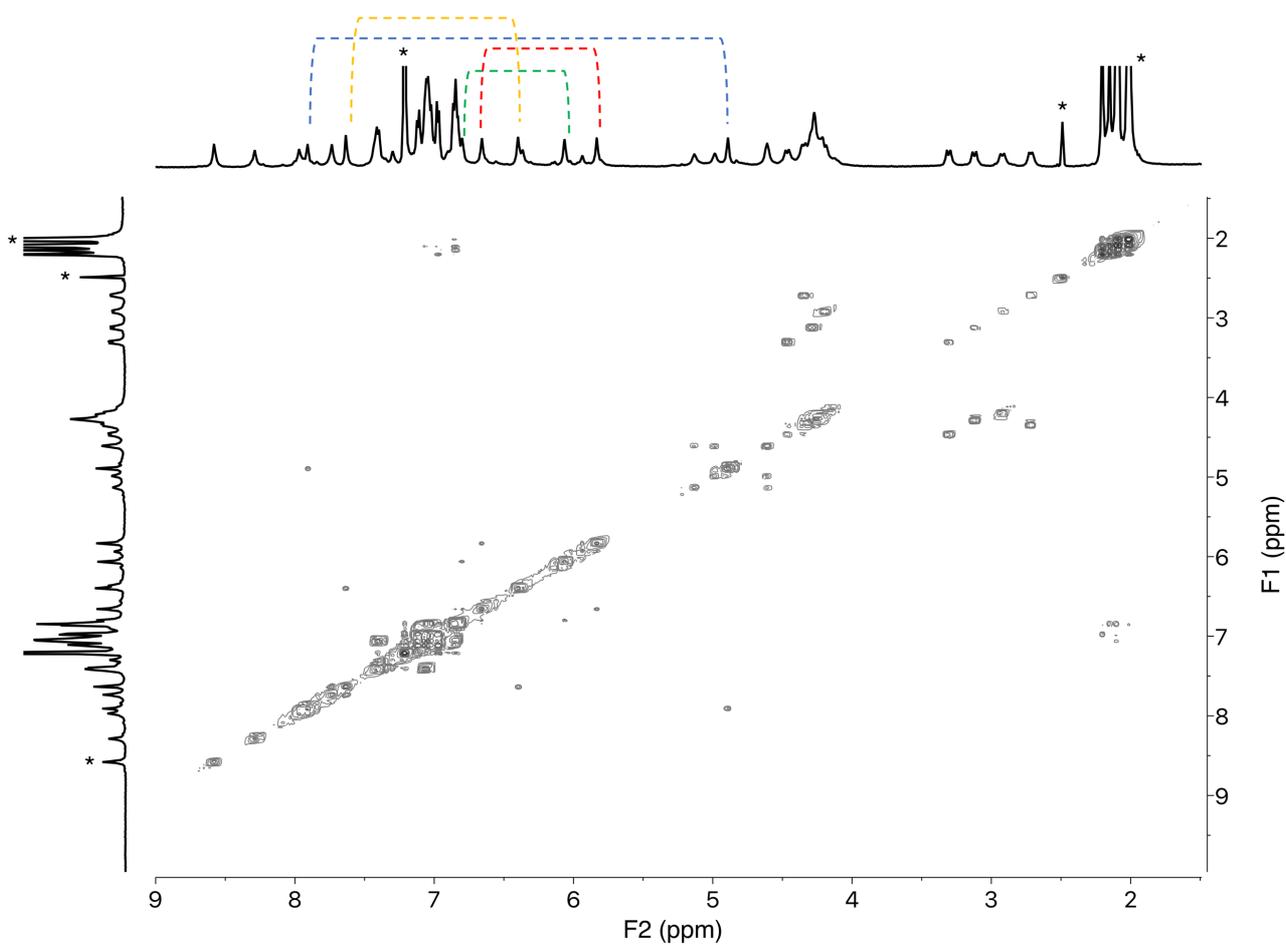
Figure S1. 2D ROESY spectrum of UC4T .....	S2
Figure S2. DOSY plot of [UC4T] = 1 mM in CDCl <sub>3</sub> /DMSO- <i>d</i> <sub>6</sub> 94:6 .....	S3
Figure S3. COSY spectrum of [UC4T] = 1 mM in CDCl <sub>3</sub> /DMSO- <i>d</i> <sub>6</sub> 98:2. ....	S4
Figure S4. HSQC spectrum of [UC4T] = 1 mM in CDCl <sub>3</sub> /DMSO- <i>d</i> <sub>6</sub> 98:2. ....	S5
Figure S5. Section of the NOESY spectrum of [UC4T] = 1 mM in CDCl <sub>3</sub> /DMSO- <i>d</i> <sub>6</sub> 98:2. ....	S6
Figure S6. VT NMR analysis (500 MHz) of [UC4T] = 1 mM in CDCl <sub>3</sub> /DMSO- <i>d</i> <sub>6</sub> 98:2. ....	S7
Figure S7. <sup>1</sup> H NMR spectra of a) [UC4T] = 1 mM in CDCl <sub>3</sub> /DMSO- <i>d</i> <sub>6</sub> 98:2 with K <sup>+</sup> or Ba <sup>2+</sup> . ....	S8
X-ray structure refinement details of the α and β forms of UC4T .....	S9
Figure S8. Asymmetric units with anisotropic ellipsoids of α and β forms of UC4T.....	S9
Table S1. Crystal data and structure refinement for α and β forms of UC4T .....	S10
Conformations of the ureido arms in α and β crystal forms of UC4T .....	S11
Table S2. Orientation of the ureido arms for the α and β crystal forms of UC4T.....	S11
Crystal Packing in α and β crystal forms of UC4T .....	S12
Figure S9. Assembly of 1D array of UC4T molecules in the β form. ....	S13
Figure S10. Crystal packing of the triclinic α and monoclinic β forms of UC4T. ....	S14
Figure S11. Solvent channel observed in the β form of UC4T.....	S15
Figure S12. Solvent cavities observed in the α form of UC4T. ....	S15



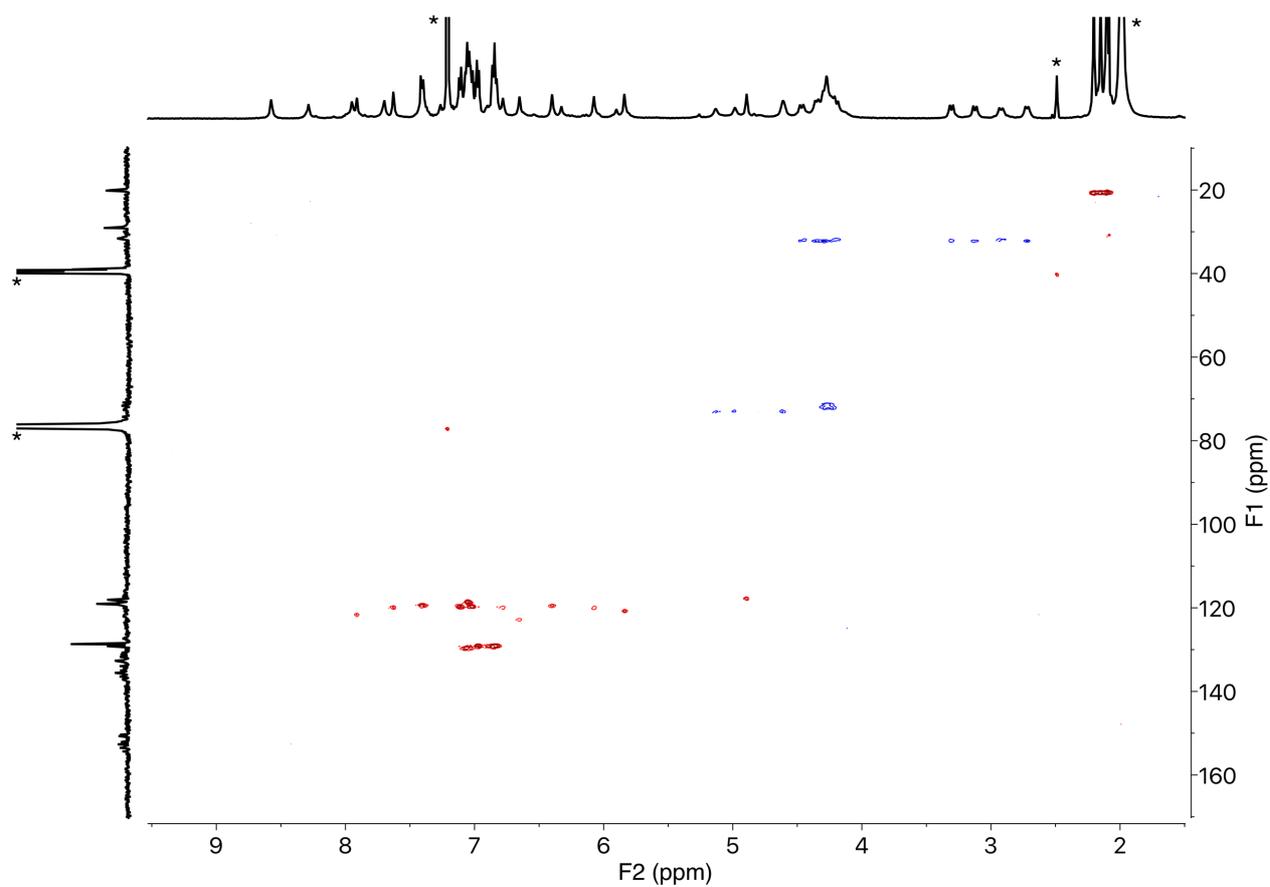
**Figure S1.** 2D ROESY spectrum of UC4T (500 MHz, DMSO-*d*<sub>6</sub>, 298 K), mixing time 400 ms. The asterisks indicate the residual peaks of the solvents.



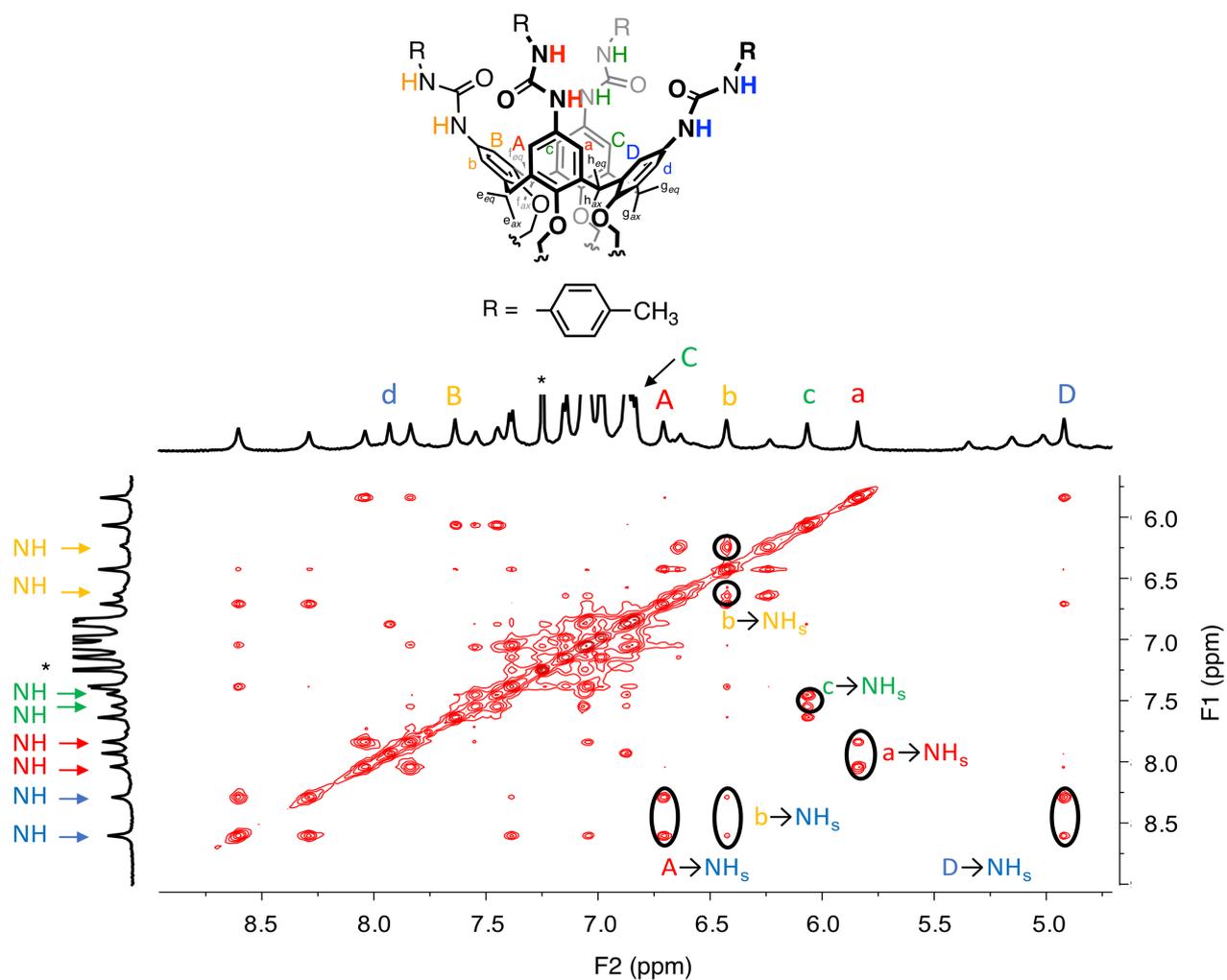
**Figure S2.** DOSY plot of [UC4T] = 1 mM in  $\text{CDCl}_3/\text{DMSO-}d_6$ , 94:6. The asterisks indicate the residual peaks of the solvents.



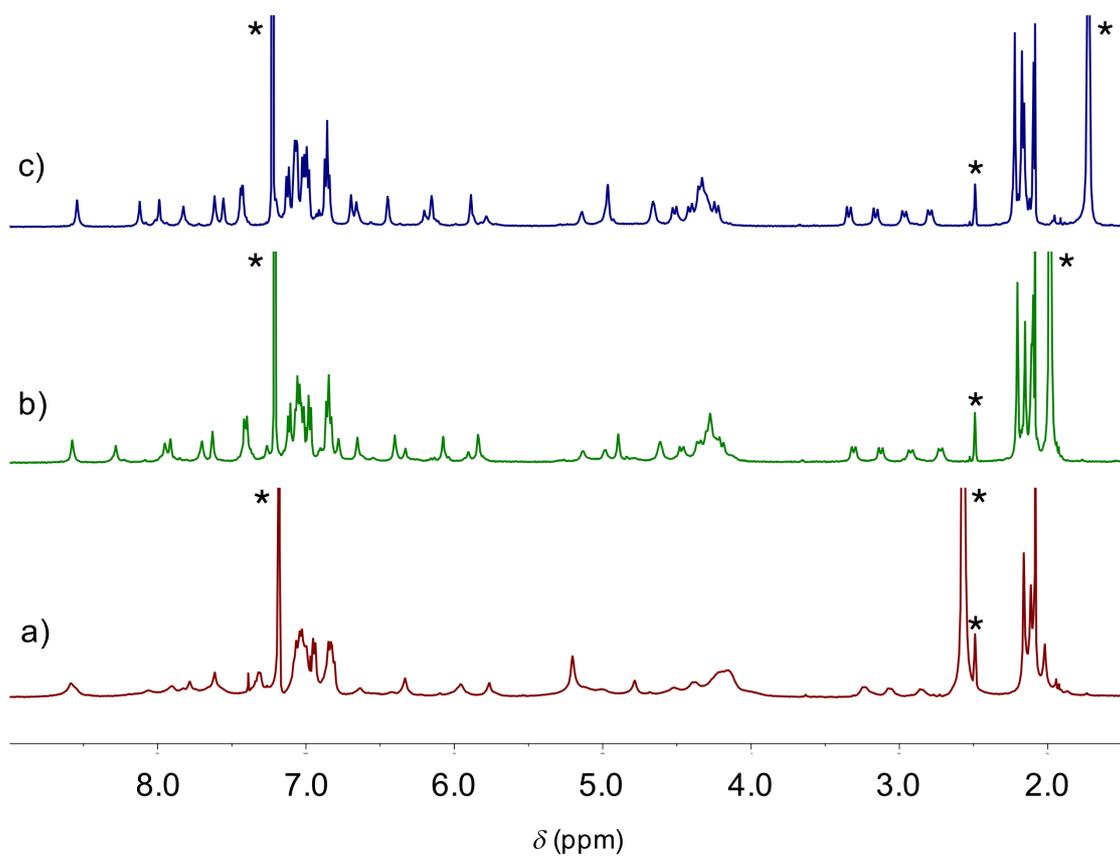
**Figure S3.** COSY spectrum (500 MHz, 298 K) of [UC4T] = 1 mM in CDCl<sub>3</sub>/DMSO-*d*<sub>6</sub>, 98:2. The asterisks indicate the residual peaks of the solvents.



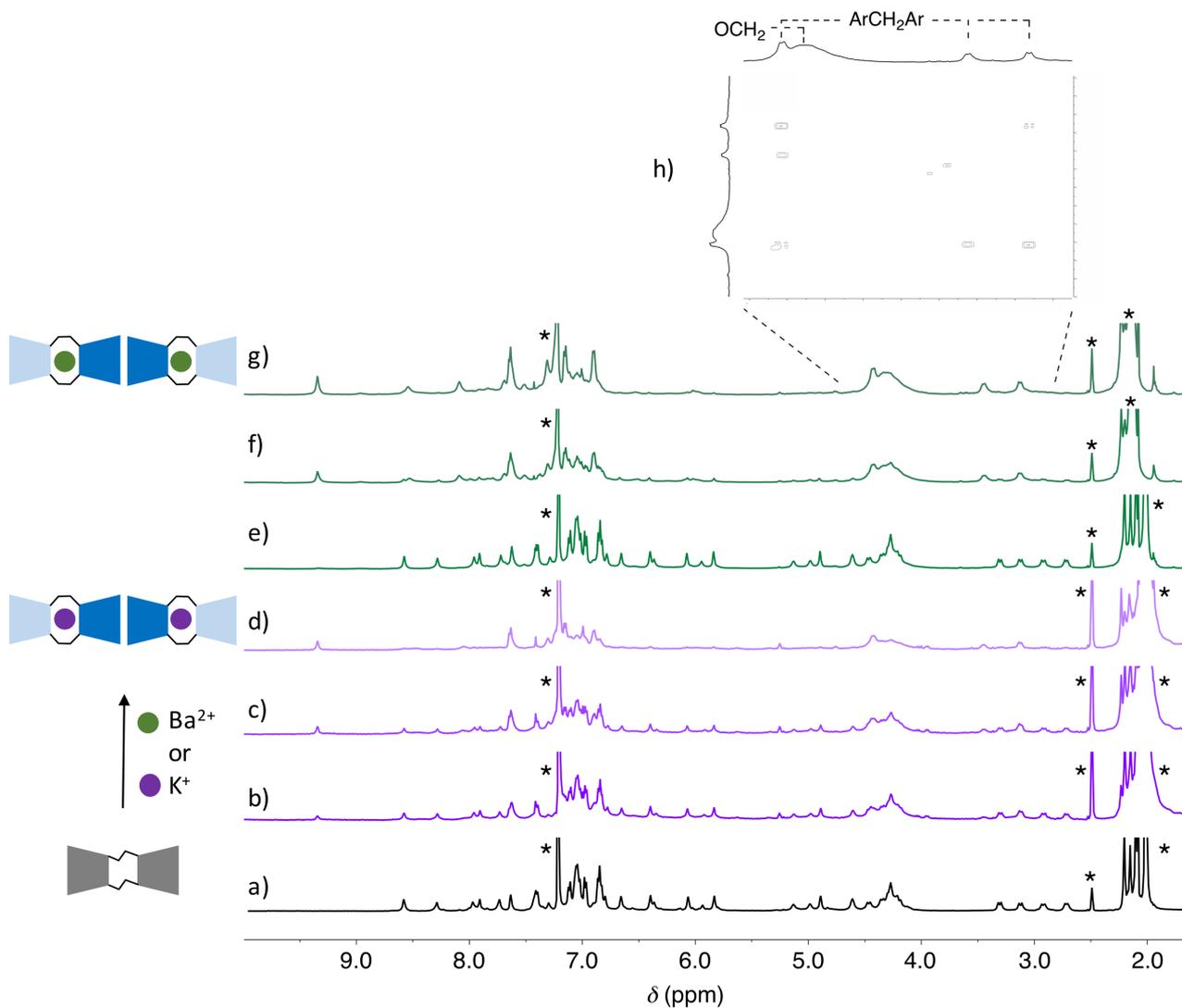
**Figure S4.** HSQC spectrum of [UC4T] = 1 mM in CDCl<sub>3</sub>/DMSO-*d*<sub>6</sub>, 98:2. The asterisks indicate the residual peaks of the solvents.



**Figure S5.** Section of the NOESY spectrum (500 MHz, 298 K) of [UC4T] = 1 mM in CDCl<sub>3</sub>/DMSO-*d*<sub>6</sub>, 98:2.



**Figure S6.** VT NMR analysis (500 MHz) of [UC4T] = 1 mM in CDCl<sub>3</sub>/DMSO-*d*<sub>6</sub>, 98:2 at: a) 328 K; b) 298 K and c) 243 K. The asterisks indicate the residual peaks of the solvents.

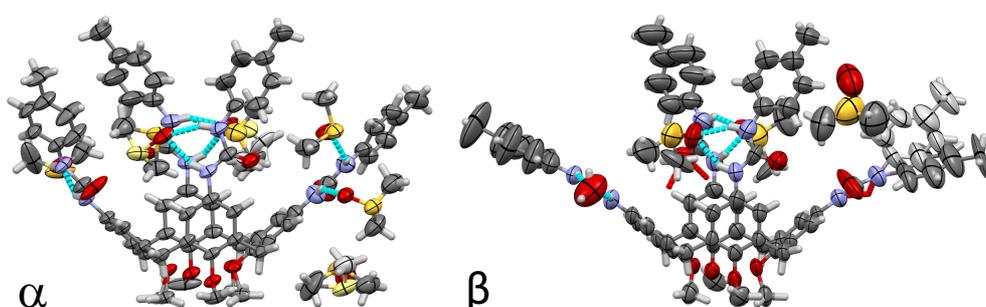


**Figure S7.**  $^1\text{H}$  NMR spectra (500 MHz, 298 K) of: a)  $[\text{UC4T}] = 1 \text{ mM}$  in  $\text{CDCl}_3/\text{DMSO-}d_6$ , 98:2; b) 1 day after addition of KI; c) 3 days after addition of KI; d) 7 days after addition of KI; e) 1 day after addition of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ; f) 7 days after addition of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ; g) 14 days after addition of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ; h) section of the COSY spectrum of **UC4T** 14 days after addition of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . The asterisks indicate the residual peaks of the solvents.

## X-ray structure refinement details of the $\alpha$ and $\beta$ forms of UC4T

The asymmetric unit of the triclinic  $\alpha$  form (P-1 space group) contains a half **UC4T** molecule located on a center of crystallographic symmetry, with 4.6 co-crystallized DMSO molecules located in 6 different crystallographic independent sites with partial occupancy factors (Figure S8). Three of these solvent molecules also show a two-position disorder. Furthermore, two central ethylene linking groups of **UC4T** relate by a center of symmetry show two-position disorder.

The monoclinic  $\beta$  form (C 2/c space group) also shows the **UC4T** molecules located on crystallographic inversion centers. One terminal aryl group was found to be disordered over two almost orthogonal positions. Three different sites of co-crystallized DMSO molecules (for a total of 1.8 molecules) and one water molecule were modelled in the asymmetric unit of the electron density maps (Figure S8). This crystal form is characterized by large solvent channels (15% of cell volume) partially filled by highly disordered solvent molecules. The diffused residual electron density present in these channels was corrected by the SQUEEZE procedure.<sup>1</sup> In these channels a total of 678 electrons per unit cell were found. This corresponds to about two further disordered DMSO molecules per asymmetric unit. Crystallographic data are reported in Table S1.



**Figure S8.** Asymmetric unit with anisotropic ellipsoid representation of non-H atoms of  $\alpha$  and  $\beta$  forms of **UC4T**. Ellipsoids are shown at the 50% probability level. The atom species are in CPK colours with alternative positions of disordered groups in paler colours. H-bonds are evidenced with dashed lines.<sup>16</sup>

<sup>1</sup> Spek, A. L. PLATON SQUEEZE: A tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallogr. Sect. C Struct. Chem.* 2015, **71**, 9–18.

**Table S1.** Crystal data and structure refinement for  $\alpha$  and  $\beta$  forms of **UC4T**

	$\alpha$	$\beta$
Empirical formula	C <sub>128</sub> H <sub>120</sub> N <sub>16</sub> O <sub>16</sub> , 9.2(C <sub>2</sub> H <sub>6</sub> O S)	C <sub>128</sub> H <sub>120</sub> N <sub>16</sub> O <sub>16</sub> , 7.6(C <sub>2</sub> H <sub>6</sub> O S), 2(H <sub>2</sub> O)
Formula weight	2857.17	2768.19
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.7	1.0
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>C</i> 2/c
Unit cell dimensions (Å, °)	<i>a</i> = 12.729(9) <i>b</i> = 15.650(3) <i>c</i> = 19.849(5) $\alpha$ = 91.255(5) $\beta$ = 91.14(3) $\gamma$ = 103.68(3)	<i>a</i> = 40.093(14) <i>b</i> = 22.414(5) <i>c</i> = 18.799(3) $\alpha$ = 90 $\beta$ = 107.521(12) $\gamma$ = 90
Volume (Å <sup>3</sup> )	3840(3)	16110(7)
Z	1	4
$\rho_{\text{calcd}}$ (g/cm <sup>3</sup> )	1.236	1.141
$\mu$ (mm <sup>-1</sup> )	0.193	0.393
F(000)	1514	5869
Reflections collected	81832	16433
Independent reflections	15039	6028
Data / restraints / parameters	15039 / 0 / 1019	6028 / 1336 / 794
GooF	1.007	1.104
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.1228 w <i>R</i> <sub>2</sub> = 0.3307	<i>R</i> <sub>1</sub> = 0.1409 w <i>R</i> <sub>2</sub> = 0.3645
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1570 w <i>R</i> <sub>2</sub> = 0.3693	<i>R</i> <sub>1</sub> = 0.1539 w <i>R</i> <sub>2</sub> = 0.3809
CCDC code	2299675	2299676

## Conformations of the ureido arms in $\alpha$ and $\beta$ crystal forms of UC4T

Table S2 shows details of the different orientations and deformations of the ureido arms in the two crystal forms. The tilt of the ureido groups with respect to the corresponding calix-aryl moieties and with respect to the terminal aryl group is more regular in the  $\alpha$  form. These values range from 12.2 to 28.2° in the  $\alpha$  form and from 6.0 to 58.0° in the  $\beta$  form (Table S2). A significant bend of one arm toward the calix cup is observed in the  $\alpha$  form, as indicated by the -2.68 Å out of plane distance of the terminal methyl group from the aromatic plane of the corresponding calix aryl group. The  $\beta$  form shows three arms bent significantly outward (Table S2). The partial loss of planarity of these aromatic systems is highly influenced by the intermolecular H-bond formation and crystal packing.

**Table S2.** Orientation of the ureido arms for the  $\alpha$  and  $\beta$  crystal forms of **UC4T**. Dihedral angles between the planar ureido group and the aromatic rings of the phenolic and *p*-tolyl groups to which they are attached and between the corresponding aromatic rings. Out of plane distance of the terminal methyl group from the aromatic plane of the corresponding phenolic group. The negative (positive) sign indicates an inward (outward) bend of the arm with respect to the calix cup.

crystal form <sup>a</sup>	ureido – phenolic (°)	ureido – <i>p</i> -tolyl (°)	phenolic – <i>p</i> -tolyl (°)	Out of plane distance (Å)
$\alpha$ , A	17.8	14.8	32.6	0.35
$\alpha$ , B	28.2	25.9	53.2	0.79
$\alpha$ , C	12.2	28.1	37.5	-2.68
$\alpha$ , D	21.9	26.7	45.0	0.44
$\beta$ , A	6.0	10.6	16.0	1.41
$\beta$ , B	58.0	50.9	58.0	4.19
$\beta$ , C <sup>b</sup>	23.5	29.4 (47.1)	20.4 (69.5)	2.52 (-0.79)
$\beta$ , D	12.6	21.8	34.4	0.24

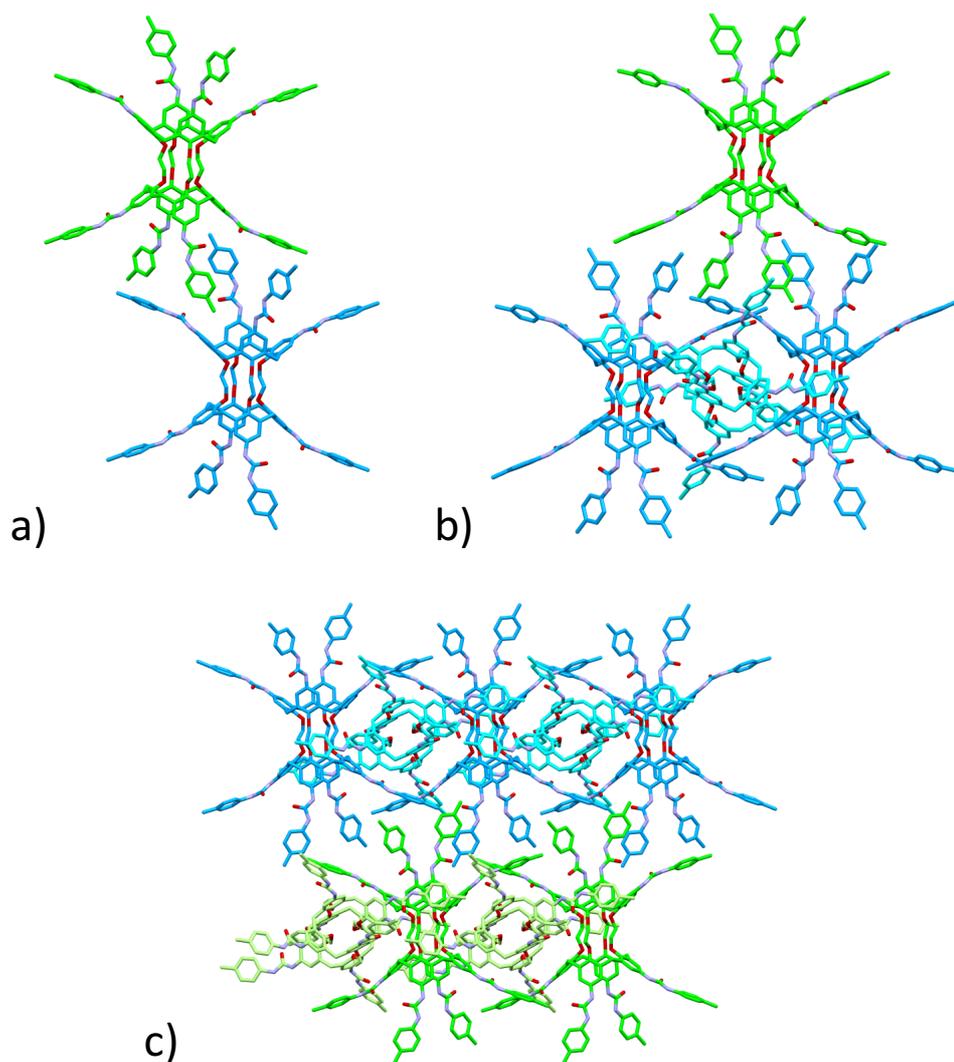
<sup>a</sup> See text.

<sup>b</sup> The values in parenthesis refer to the angles made with the second orientation of the external aryl group.

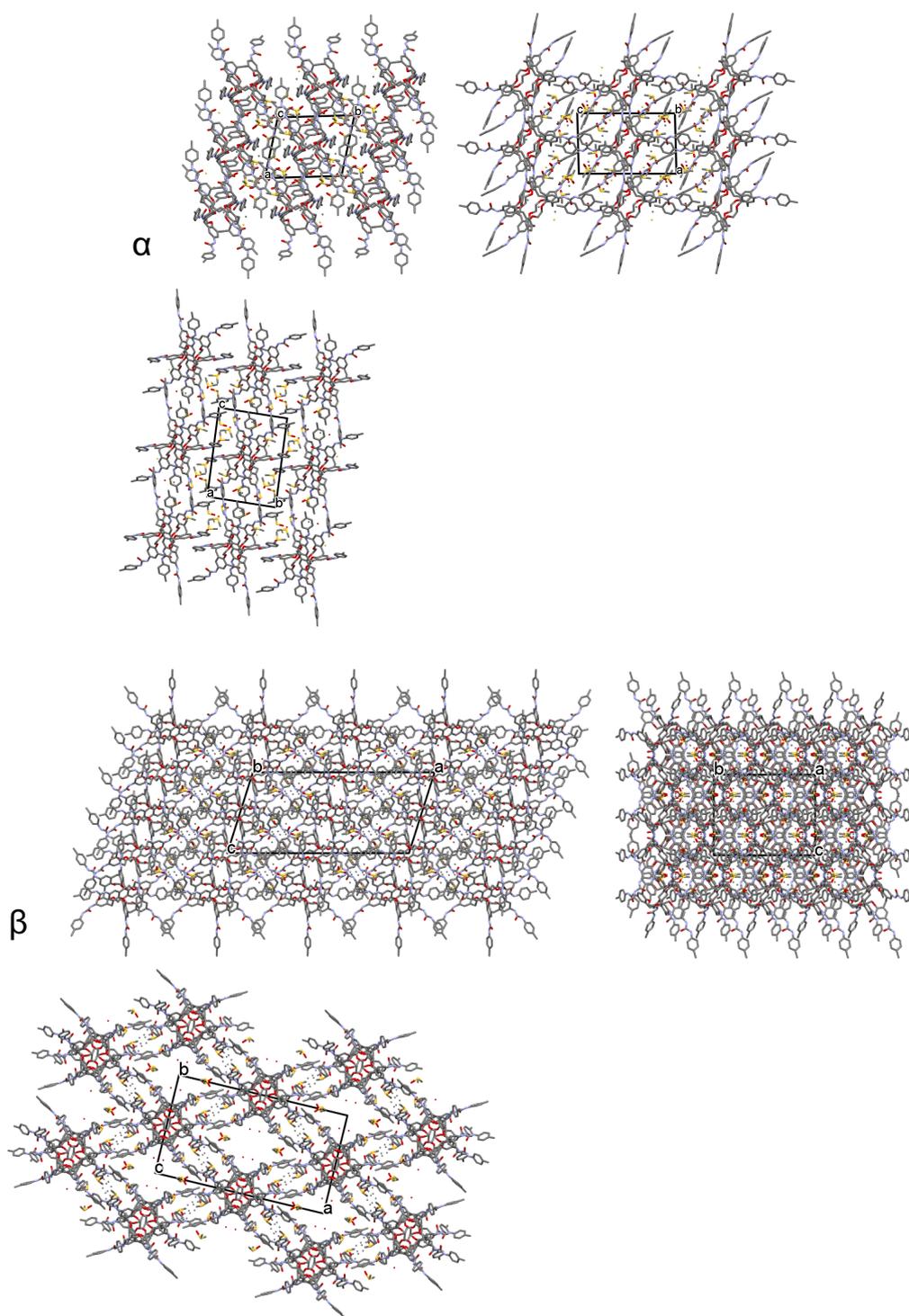
## Crystal Packing in $\alpha$ and $\beta$ crystal forms of UC4T

As outlined in the main text, in the  $\beta$  form, the bifurcated intermolecular H-bonds produce a close packed 1D array of **UC4T** molecules interconnected by a complementary H-bond network along the  $c$  axis of the unit cell. These 1D arrays of **UC4T** molecules interconnected by a complementary H-bond network, are assembled in the  $\beta$  form through an almost face to face assembly of calix-caps (Figure S9). In particular, two facing **UC4T** molecules form a pseudo capsule mainly delimited by the ureido arms of the pinched sides of the calixarene moieties (Figure S9a). However, this pseudo capsule contains a partially inserted ureido arm of an adjacent molecule (Figure S9b). Overall, adjacent 1D arrays are interconnected by these pseudo capsules, forming an interdigitation of ureido arms of the pinched calix sides of different arrays (Figure S9c). These 1D arrays are assembled in the C-centered monoclinic lattice in such a way to produce large parallel solvent channels as observed in the crystal packing of the  $\beta$  form (Figure S10, Figure S11) only partially filled by highly disordered solvent molecules. On the contrary, the  $\alpha$  form shows a more closed packing with the small cavities filled by the DMSO molecules (Figure S12).

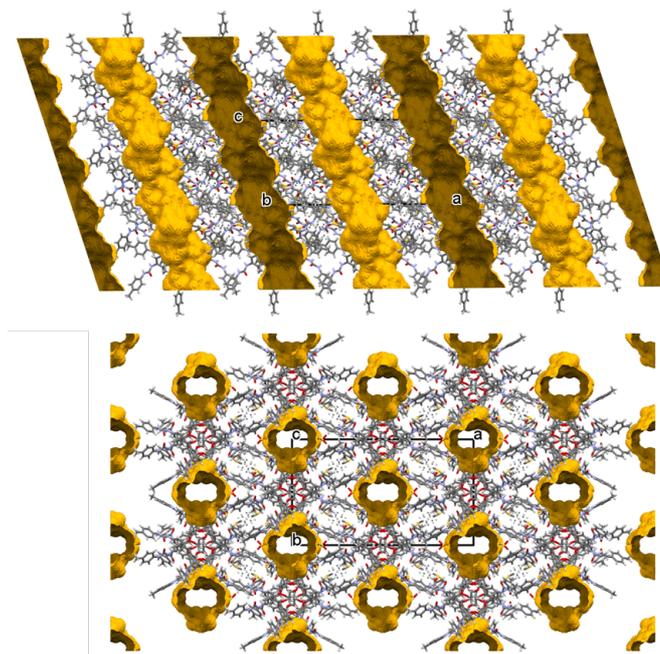
When considering the crystal packing of **UC4T** molecules exclusively (omitting solvent molecules from the structural model), the solvent accessible volume of the two crystal forms (calculated with a solvent probe radius of 1.2 Å and a grid spacing of 0.2 Å) are quite similar, accounting for 38.5 and 42.0 % of the crystal volume for  $\alpha$  and  $\beta$  forms, respectively. However, upon by including the more strongly coordinated solvent molecules H-bonded to ureido groups in the structural model, the solvent accessible volumes decrease to 6.4% and 29.1% for  $\alpha$  and  $\beta$  forms, respectively. Furthermore, with the complete structural models, which includes solvent molecules entrapped in packing cavities, the solvent accessible volumes reduce to 0.6 % and 16.1 % for  $\alpha$  and  $\beta$  forms, respectively. The residual accessible solvent volume observed in the  $\alpha$  form corresponds to spherical cavities of 12.16 Å<sup>3</sup> located in the middle of the calix cups (Figure S10). These spherical cavities are also present in the  $\beta$  form, alongside the solvent channels.



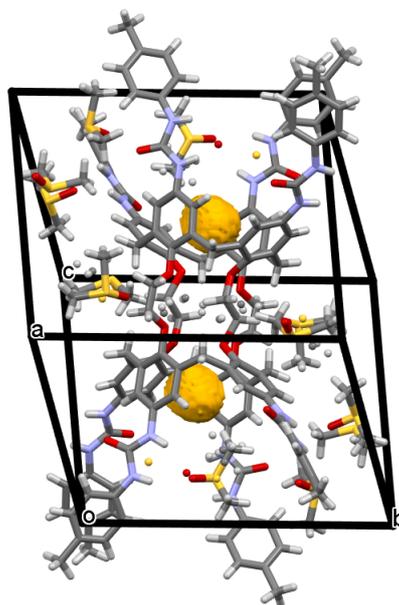
**Figure S9.** Assemblies of 1D arrays of **UC4T** molecules interconnected by a complementary H-bond network observed in the  $\beta$  form. a) Two facing **UC4T** molecules form a pseudo capsule mainly delimited by the ureido arms of the pinched sides. b) The pseudo capsule contains a partially inserted ureido arm of an adjacent molecule. c) Adjacent 1D arrays are interconnected by these pseudo capsules. Molecules of the same 1D array have the same color.



**Figure S10.** Orthogonal representation of the crystal packing of the triclinic  $\alpha$  and monoclinic  $\beta$  forms of UC4T. The projections follow the convention used for the space groups in the International Tables of Crystallography.



**Figure S11.** Side and top views of the solvent channel observed in the  $\beta$  form of **UC4T**. The solvent contact surface, calculated with a solvent probe radius of 1.4 Å (corresponding to a water molecule probe) and a grid spacing of 0.2 Å, delimitates an accessible water solvent volume corresponding to 14% of the total crystal volume.



**Figure S12.** Solvent cavities observed in the  $\alpha$  form of **UC4T**. The solvent contact surface, calculated with a solvent probe radius of 1.2 Å and a grid spacing of 0.2 Å, delimitates two symmetric spherical cavities of 12.16 Å<sup>3</sup> each located in the middle of the calix cups. They correspond to 0.6 % of the total crystal volume.