Supporting Information

SELF-ASSEMBLY OF N^3-SUBSTITUTED XANTHINES IN THE SOLID STATE AND AT THE SOLID-LIQUID INTERFACE

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1. NMR Spectroscopy and ESI study of N^3-octadecylxanthine (compound 2)

NMR spectra were recorded on a Varian Unity INOVA 600 MHz instrument equipped with a reverse probe. ESI-MS spectra were obtained with a Micromass ZMD-4000 spectrometer. Compound **2**, i.e. N^3-octadecylxanthine was fully characterized by NMR. Signals were assigned on the basis of bidimensional spectra (Figs. S1-S5). Due to its low solubility, the compound was usually dissolved in high boiling solvents (DMSO or 1,1,2,2-tetrachloroethane) by heating, to improve *s/n* ratio.

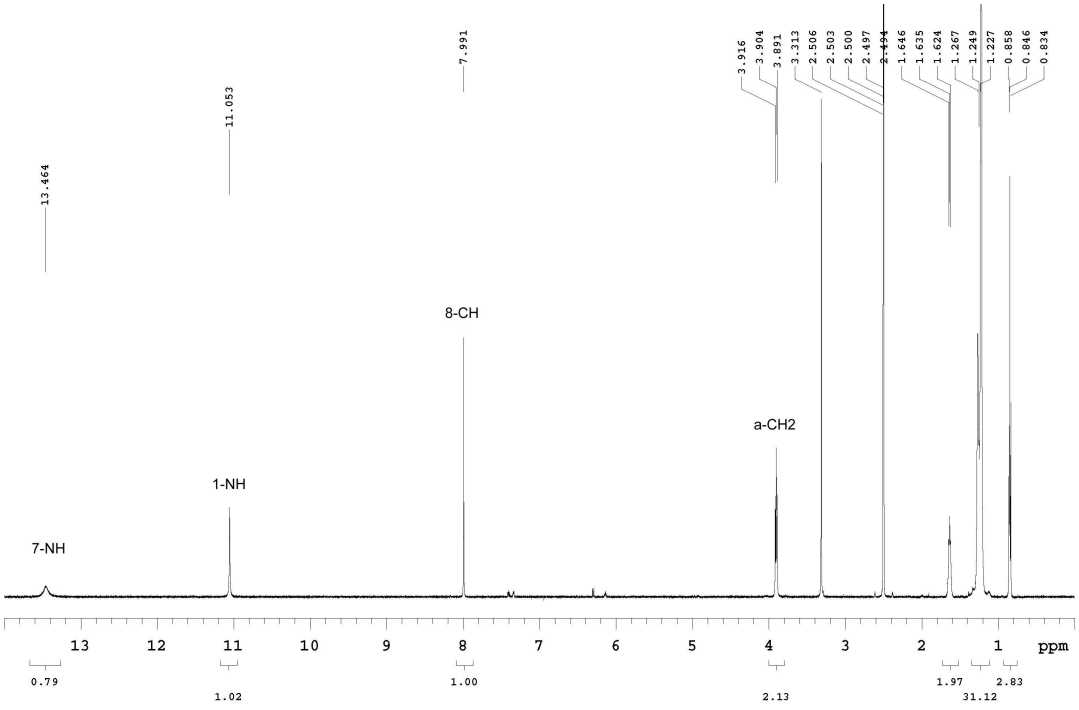

Figure S1. ^{1}H-NMR spectrum of compound **2** in DMSO-d_6 at r.t.

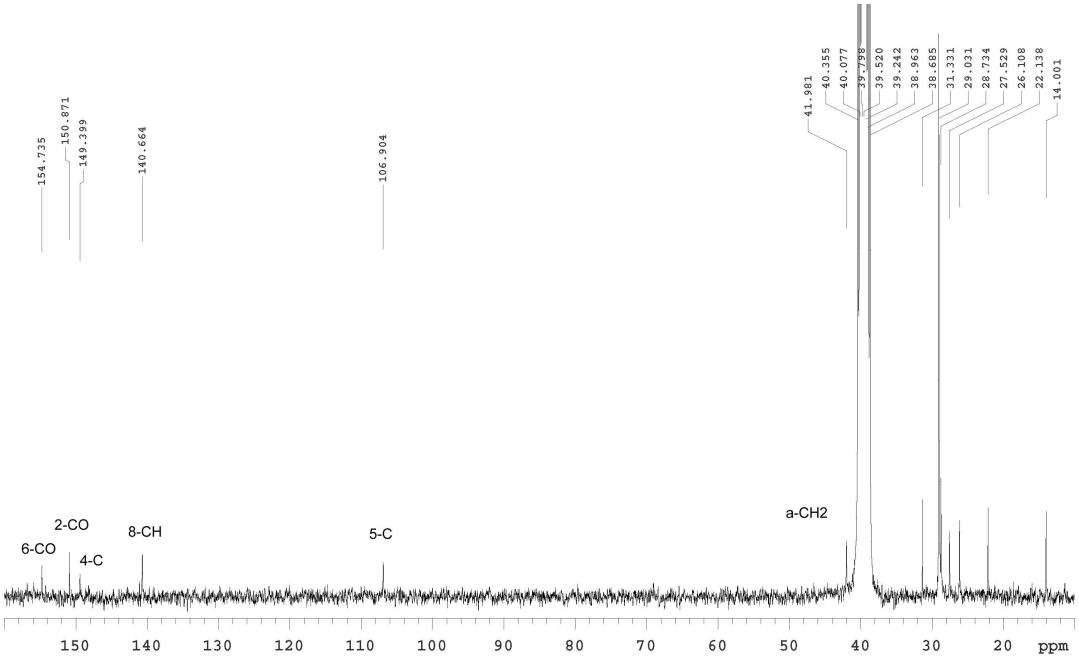

Figure S2. ^{13}C NMR spectrum of compound **2** in DMSO-d_6 at r.t.

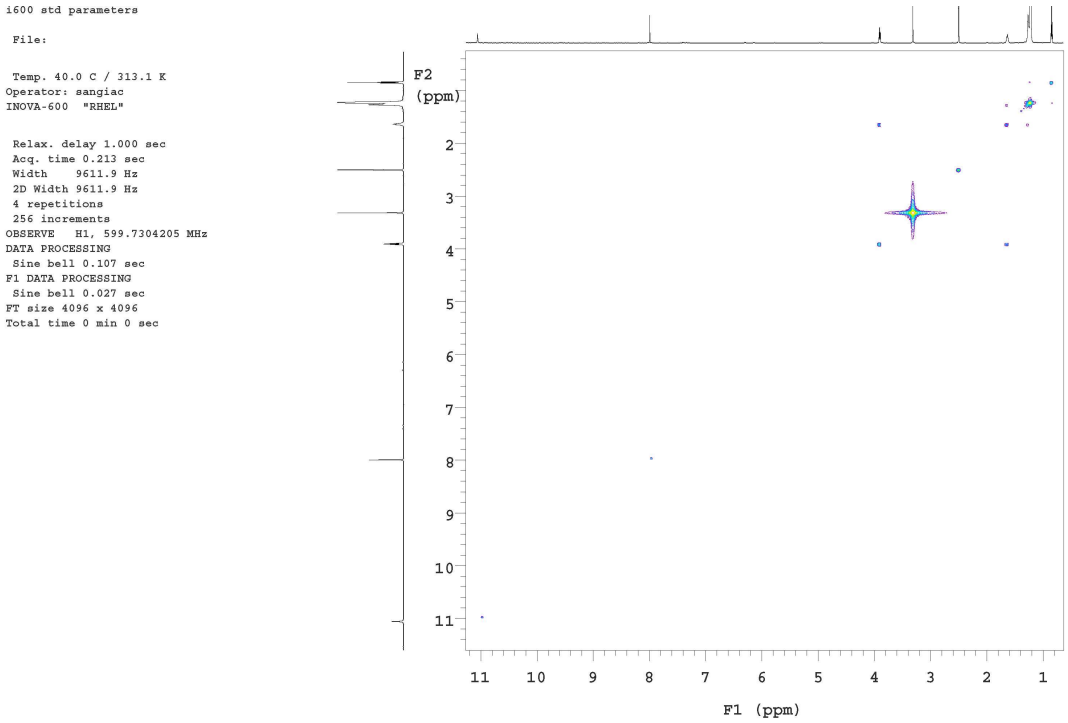

Figure S3. COSY spectrum of compound **2** in DMSO-d_6 at 40 °C

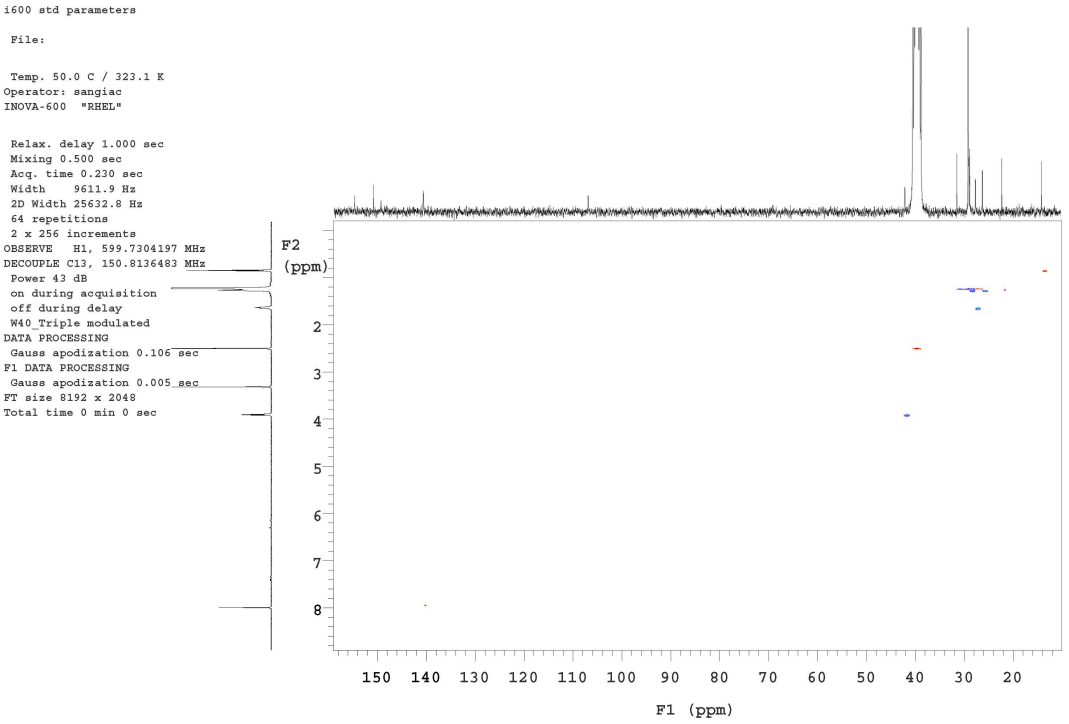

Figure S4. HSQC spectrum of compound **2** in DMSO-d_6 at 50 °C

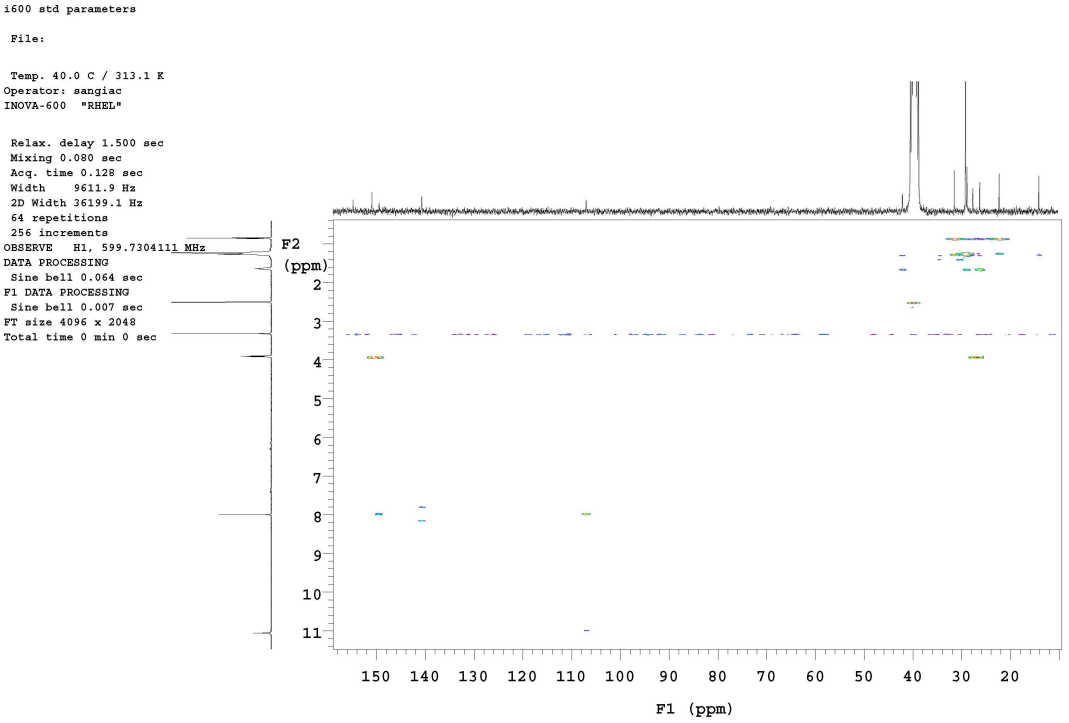

Figure S5. HMBC spectrum of compound **2** in DMSO-d_6 at 40 °C

Although no specific H-bonding pattern could be demonstrated by NMR investigations, some clues for the existence of H-bonded species (dimers or oligomers) in solution can be inferred. For instance, . 7-NH, 1-NH and H-8 peaks move upfield with temperature both in CD_2Cl_4 and in DMSO-d_6 (Fig. S6).

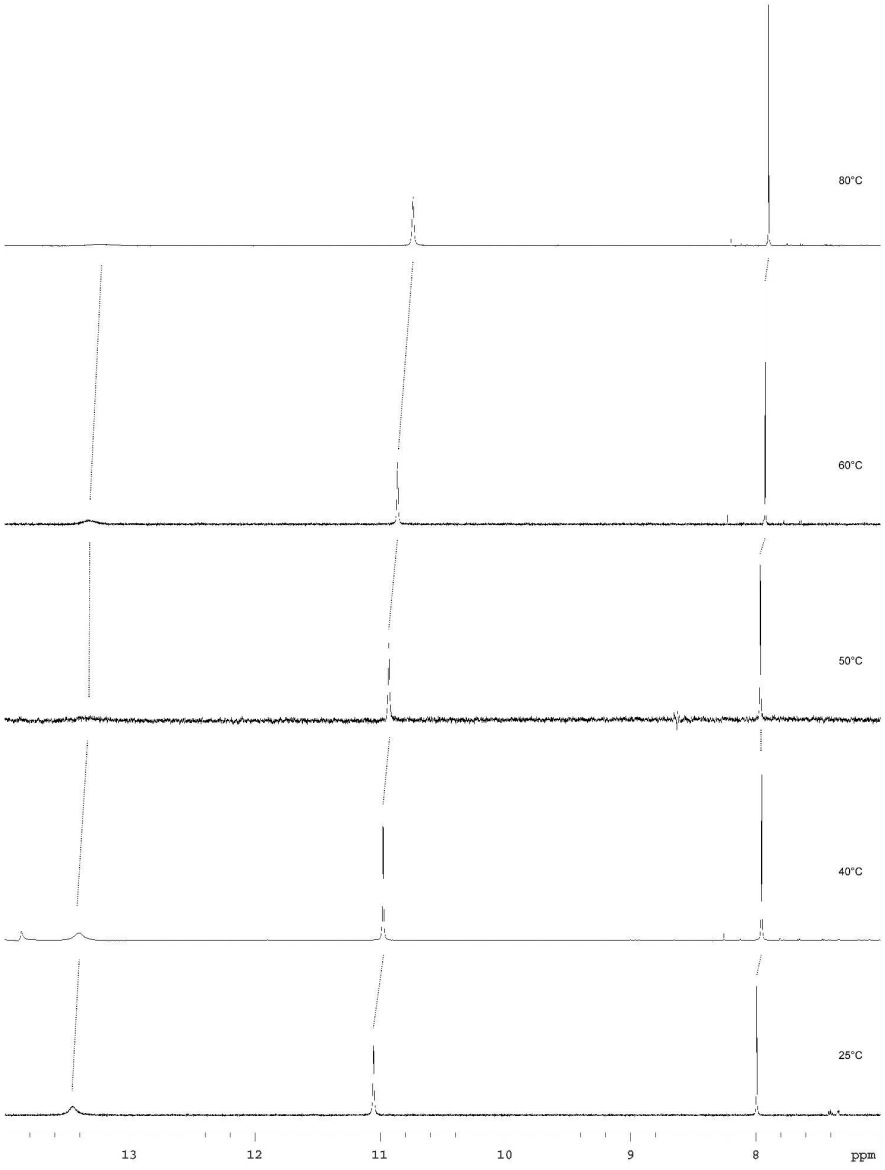

Figure S6. Downfield portion of ^{1}H-NMR spectra of compound **2** in DMSO-d_6 at different temperatures.

The ESI-MS (positive mode) spectrum of **2** in $C_2H_2Cl_4/CHCl_3$ solution shows as the main peaks signals corresponding to $[(\mathbf{2})Na]^+$, $[(\mathbf{2})_2Na]^+$, $[(\mathbf{2})_3Na]^+$ and $[(\mathbf{2})_4Na]^+$. The relative intensity of the last two peaks is indicative of the attitude of **2** to form ion-templated X-quartets (Fig. S7).

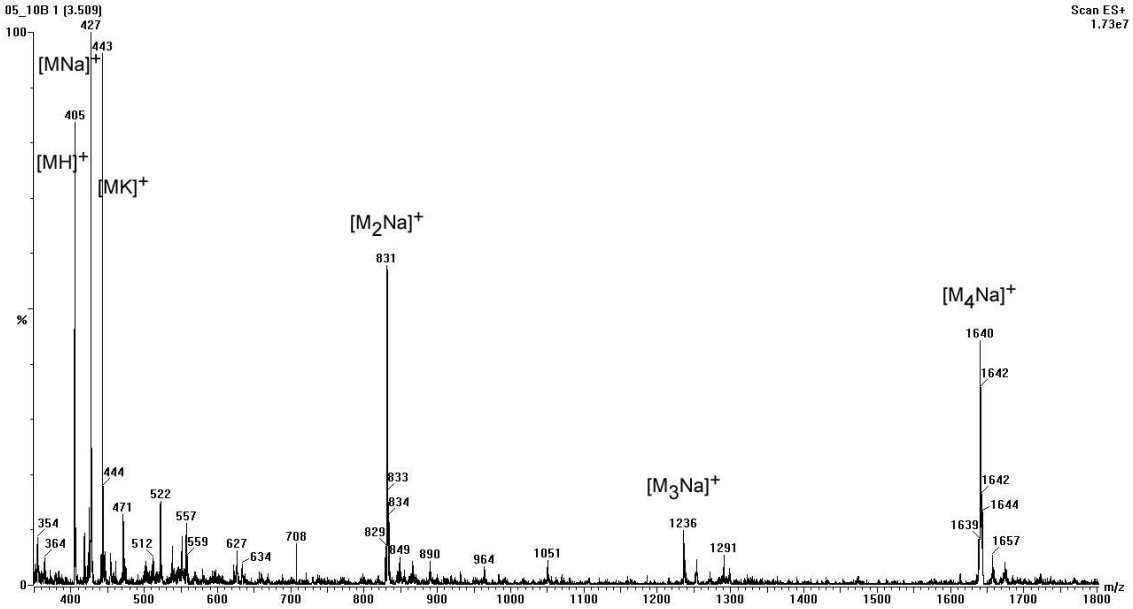

Figure S7. ESI-MS (positive mode) of compound **2** in $C_2H_2Cl_4/CHCl_3$ solution (with a small amount of formic acid added).

2. Polymeric structures based on N^9-methylguanine

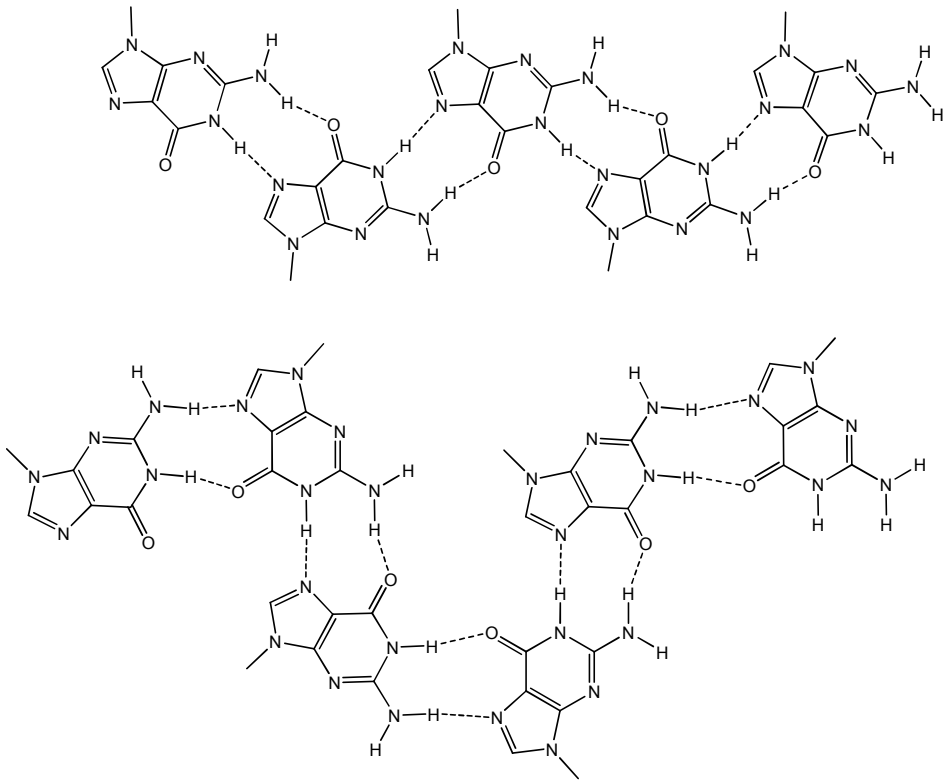

Figure S8. Schematic representation of the N^9-methylguanine in its W and U ribbon assembly.

3. X-ray powder patterns N^3-methylxanthine (compound 1)

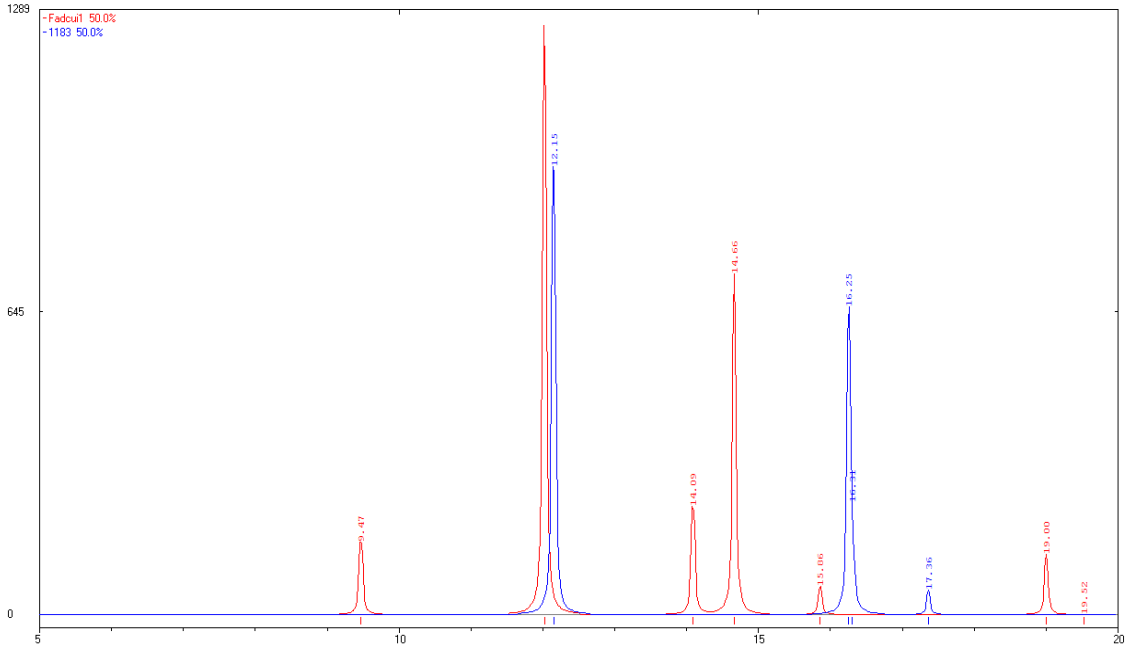

Figure S9. The calculated X-ray powder pattern for the literature (red) and the new polymorphic structure (blue) of N^3-methylxanthine (compound **1**).[1]

4. X-ray crystal structures of FADCUI and N^3-methylxanthine (1)

Table S1. Crystallographic data and structure refinement results for N^3-methylxanthine (**1**).

Name	N^3-methylxanthine
Formula	$C_6H_6N_4O_2$
Formula weight	166.15
Crystal system	Orthorhombic
Space group	$Pc2_1b$ (No. 29)
a / Å	5.449(5)
b / Å	8.160(5)
c / Å	14.558(5)
V / Å^3	647.3(7)
Z	4
D_c / g cm^{-3}	1.705
F(000)	344
μ / mm^{-1}	0.13
Reflections collected	1125
Unique reflections with I > 2σ(I),	785
Parameters refined	116
GOF on F^2	1.17
$R[F^2 > 2\sigma(F^2)]$	0.097
$wR(F^2)$	0.238
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.35, –0.37

Table S2. Bond length data for the new polymorph and the literature structure (FADCUI)[1] of N^3-methylxanthine.

	New polymorph	FADCUI
C2 - O2	1.214(9)	1.218
C2 - N3	1.367(12)	1.364
C2 - N1	1.389(10)	1.389
C4 - C5	1.324(10)	1.370
C4 - N9	1.327(10)	1.341
C4 - N3	1.392(9)	1.381
C5 - N7	1.385(9)	1.372
C5 - C6	1.457(14)	1.397
C6 - O6	1.222(10)	1.225
C6 - N1	1.373(10)	1.382
C8 - N7	1.319(12)	1.323
C8 - N9	1.344(9)	1.326
C9 - N3	1.469(9)	1.468
N1 - H1	0.86(2)	0.891
N7 - H7	0.87(2)	0.838

Table S3. Hydrogen-bond geometry of the new polymorph of N^3-methylxanthine (**1**).

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (º)
NH(1)···N(9)^{i}	0.86	2.18	3.010 (10)	163
NH(7)···O(2)^{ii}	0.87 (2)	1.97 (5)	2.774 (9)	154 (10)

Symmetry codes: (i) x+1, y+1/2, −z+1/2; (ii) −x+2, y, z−1/2.

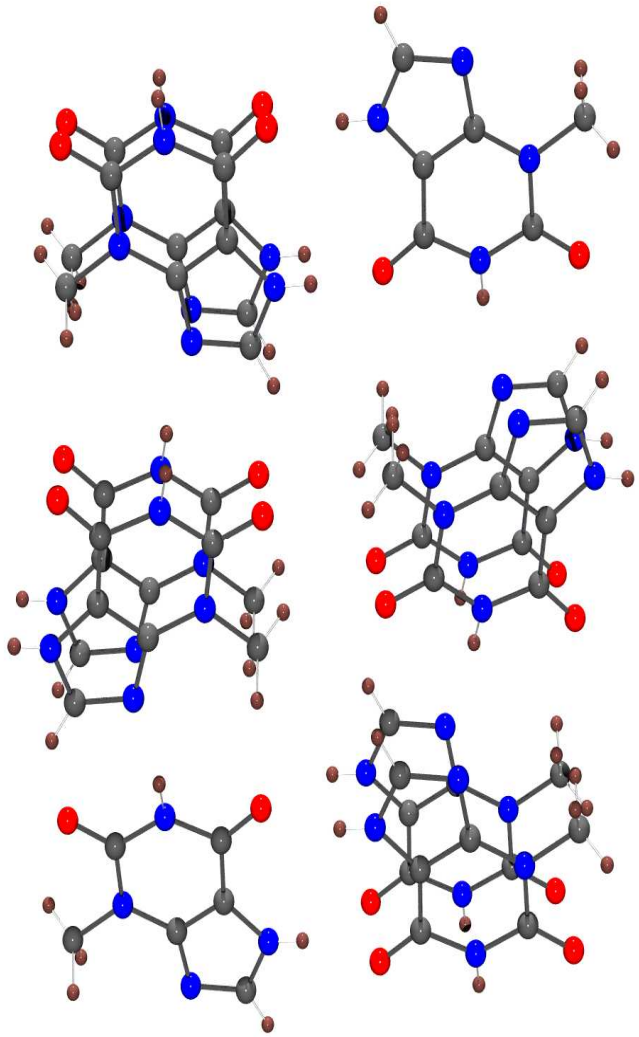

Figure S10. Stacking motif in FADCUI X-ray structure showing the parallel orientation of alternating rings. View normal to (100).

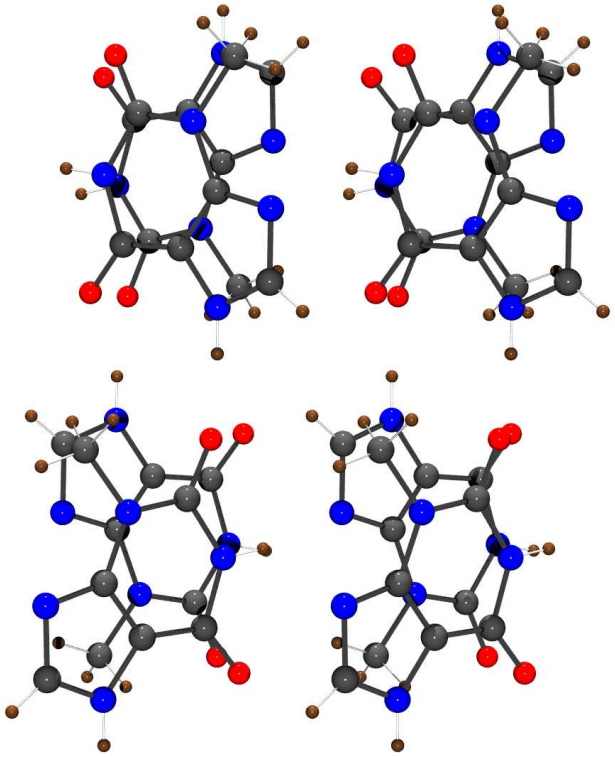

Figure S11. Stacking motif in new polymorph of **1** showing the rotated orientation of alternating rings. View normal to (010)

5. Theoretical studies

Table S4. Calculated (BLYP-D/TZ2P level of theory) total bonding energies and average H-bonding energies (in kcal/mol) of 4, 6, 8, 10 and 12 units long optimized X and G ribbons.

no. of units in ribbon	Total bonding energies (in kcal/mol)				Average stabilization energies (in kcal/mol) per H-bond.			
	X-W	**X**-U	**G**-W	**G**-U	**X**-W	**X**-U	**G**-W	**G**-U
4	-58.5	-57.7	-66.1	-64.8	-9.8	-9.6	-11	-10.8
6	-95.2	-95.2	-114.3	-116.5	-9.5	-9.5	-11.4	-11.7
8	-131.7	-128	-162.9	-165.3	-9.4	-9.1	-11.6	-11.8
10	-169.1	-169.6	-211.8	-213.7	-9.4	-9.4	-11.8	-11.9
12	-204.9	-205.3	-260.5	-262.5	-9.3	-9.3	-11.8	-11.9

X – N^3-methylxanthine, G – N^9-methylguanine, W and U – types of H-bonded ribbon.

References:

1. Low, J. N.; Tollin, P.; Brand, E.; Wilson, C. C., Structure of 3-Methylxanthine. *Acta Cryst. Sect. C* **1986,** 42, 1447-1448.