Electronic Supplementary Informations

By Artur Ciesielski,[a] Rosaria Perone,[b] Silvia Pieraccini,[b] Gian Piero Spada [b*] and Paolo Samorì [a,*]

[a] *Institut de Science et d'Ingénierie Supramoléculaires, Université de Strasbourg & CNRS 7006, Strasbourg (France). Email : samori@unistra.fr*

[b] *Alma Mater Studiorum - Università di Bologna, Dipartimento di Chimica Organica "A. Mangini",*

Via S. Giacomo 11, 40126 Bologna (Italy). Email : gianpiero.spada@unibo.it

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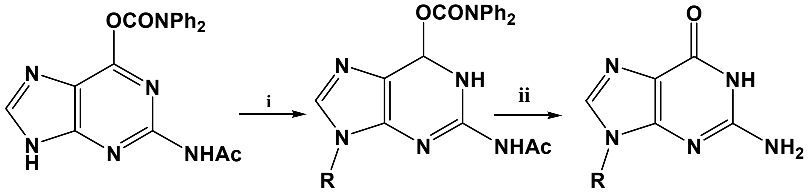
1.Synthesis of 9-Alkylguanines

General note. 9-Ethylguanine **1** was purchased from Aldrich Chemical Co. Reagents and solvents (including dry solvents) were purchased from Aldrich Chemical Co (Aldrich or Fluka catalogues) and used without any further purification, unless otherwise noted. Mass spectra were obtained using electrospray (ES) ionization with a MicroMass ZMD 4000 instrument. NMR spectra were recorded on Varian Inova (400 MHz or 600MHz) instruments.

General procedure

The preparation of protected guanine **A** has been described in ref. (S-1) . Mitsunobu coupling of **A** with alcohols (**a-h**) was carried out according to the procedure described in ref. (S-2). Details of preparation of 9-Octadecylguanine **9** and its characterisation have been described in ref. (S-3)



A B C

i (a-h)/PPh_3/THF dry/reflux
ii Ammonia/MeOH/60°

a) $C_6H_{13}OH$	**R**=C_6H_{13} (**2**)
b) $C_7H_{15}OH$	**R**=C_7H_{15} (**3**)
c) $C_8H_{17}OH$	**R**=C_8H_{17} (**4**)
d) $C_{10}H_{21}OH$	**R**=$C_{10}H_{21}$(**5**)
e) $C_{12}H_{25}OH$	**R**=$C_{12}H_{25}$(**6**)
f) $C_{14}H_{29}OH$	**R**=$C_{14}H_{29}$(**7**)
g) $C_{16}H_{33}OH$	**R**=$C_{16}H_{33}$(**8**)
h) $C_{18}H_{37}OH$	**R**=$C_{18}H_{37}$(**9**)

Protected guanine **A** (1.1mmol) was added to a solution of primary alcohol (1.15 mmol) and PPh_3 (302 mg, 1.15 mmol) in anhydrous THF (20 mL) under N_2 atmosphere. DIAD was added to the resulting suspension (231 mg, 1.15mmol).

The reaction mixture was stirred at 70°C for 6 hrs; then a second equivalent of alcohol (1.15 mmol), PPh_3 (302 mg, 1.15 mmol) and DIAD (231 mg, 1.15 mmol) were added. The mixture was stirred for further 6 hrs at the same temperature. After cooling down, the reaction mixture was poured into a saturated sodium chloride solution (25 mL) and extracted with dichloromethane (3x50 mL). The combined organic layers were washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the crude reaction mixture was purified by chromatography on silica gel affording the protected N-9 alkylated guanine **B**.

The protected N-9 alkylated guanine (0,20 mmol) was dissolved in a mixture of 30% ammonia/methanol (1:1) (60 mL). The resulting solution was heated at 60°C for 2 hrs. The solvent was then removed under reduced pressure and the crude reaction mixture was purified by chromatography on silica gel to give the expected N-9 alkylguanine **C** as a white solid.

9-Hexylguanine (2)

The general procedure described above was followed. Petroleum ether/ethyl acetate 1:1 was used for the purification of the protected N-9 hexylguanine. Dichloromethane/methanol 98:2 was used for the purification of the title compound. 42% yield.

ESI-MS: *m/z (%)*: 234.1 (100) [1-H]$^-$

Elemental analysis calcd (%) for $C_{11}H_{17}N_5O$: C 56.15, H 7.28, N 29.76; found: C 56.02, H 7.27, N 29.76.

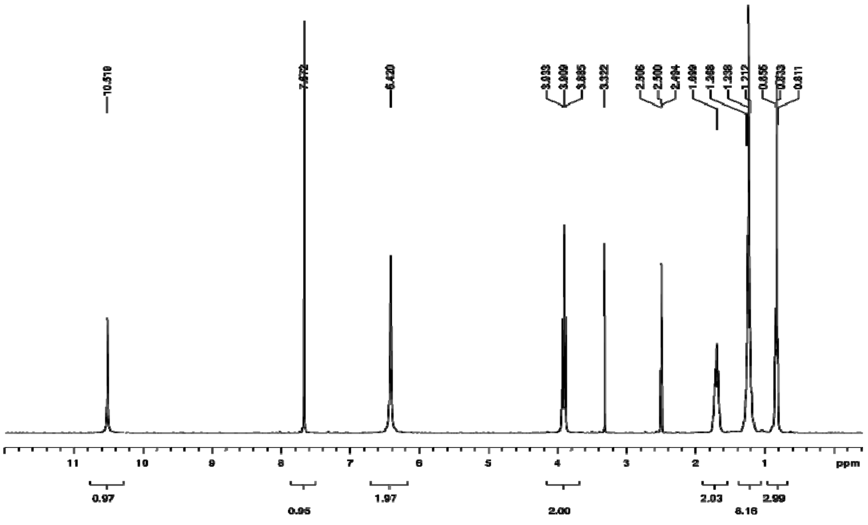


Figure S1: ^{1}H-NMR spectrum (400 MHz) of **2** in DMSO-d_6

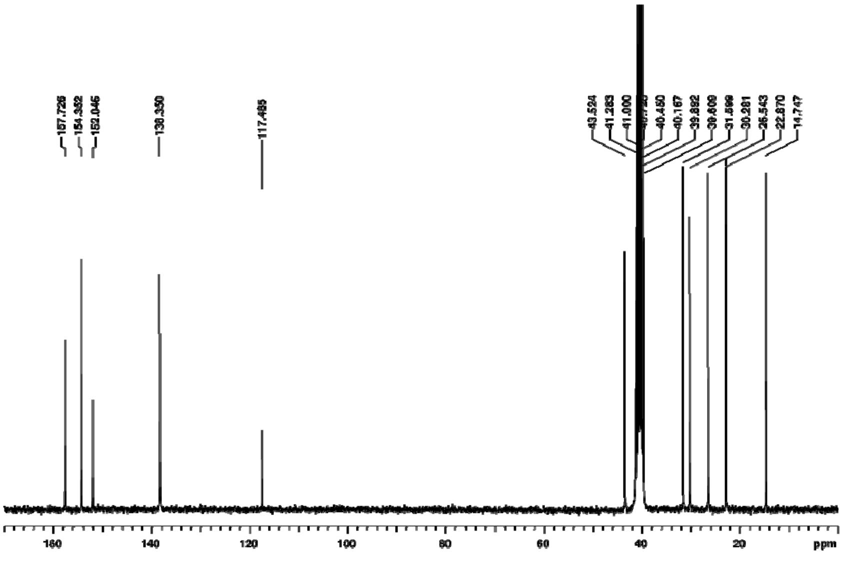


Figure S2: ^{13}C-NMR spectrum (400 MHz) of **2** in DMSO-d_6

9-Heptylguanine (3)

The general procedure described above was followed. Petroleum ether/ethyl acetate 6:4 was used for the purification of the protected N-9 heptyl guanine. Dichloromethane/methanol 94:6 was used for the purification of the title compound. 34% yield.

ESI-MS: *m/z (%)*: 248.1(100) [1-H]$^-$
Elemental analysis calcd (%) for $C_{12}H_{19}N_5O$: : C 57.81, H 7.68, N 28.09; found: C 57.94, H 7.69, N 28.16.

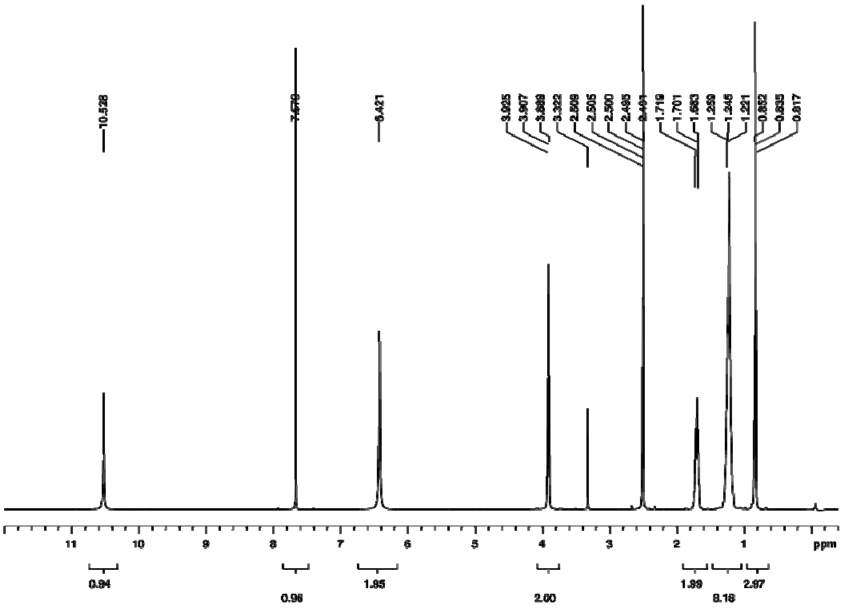


Figure S3:^{1}H-NMR spectrum (400 MHz) of **3** in DMSO-d_6

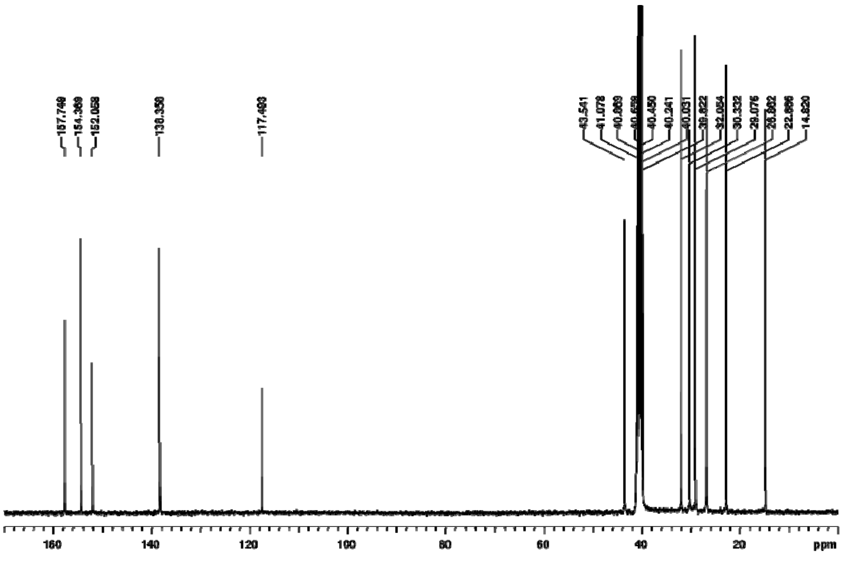


Figure S3:^{13}C-NMR spectrum (400 MHz) of **3** in DMSO-d_6

9-Octylguanine (4)

The general procedure described above was followed. Petroleum ether/ethyl acetate 6:4 was used for the purification of the protected N-9 octyl guanine. Dichloromethane/methanol 94:6 was used for the purification of the title compound. 20% yield.

ESI-MS: *m/z (%)*: 262.1 (100) [1-H]$^-$
Elemental analysis calcd (%) for $C_{13}H_{21}N_5O$: C 59.29, H 8.04, N 26.59; found: C 59.43, H 8.02, N 26.54.

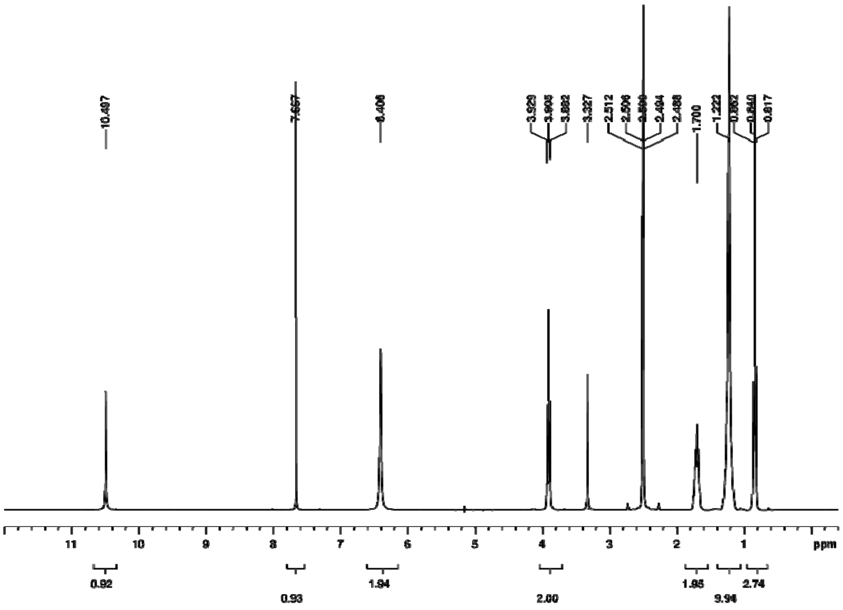


Figure S4:^{1}H-NMR spectrum (400 MHz) of **4** in DMSO-d$_6$

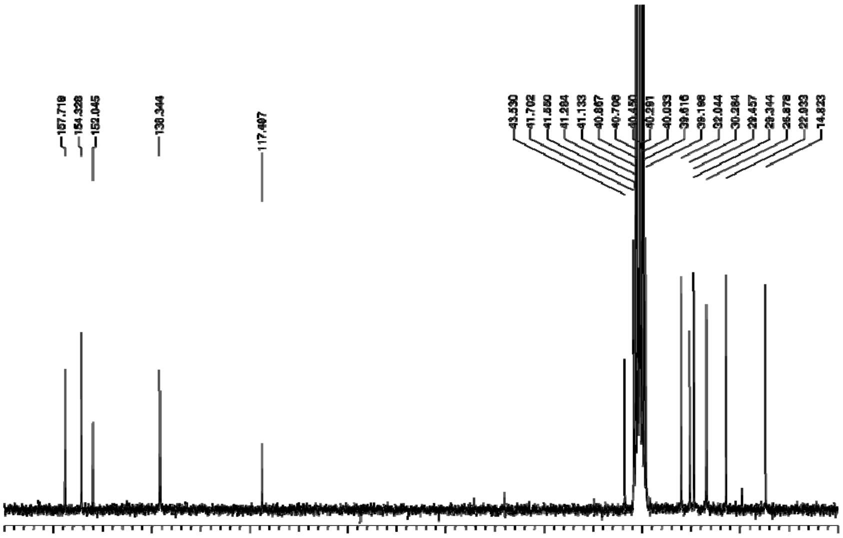


Figure S5:^{13}C-NMR spectrum (400 MHz) of **4** in DMSO-d

9-Decylguanine (5)

The general procedure described above was followed. Petroleum ether/ethyl acetate 1:1 was used for the purification of the protected N-9 decyl guanine.The title compound. was obtained trough recristallyzation from methanol. 51% yield.

ESI-MS: *m/z (%)*: 290.1 (100) [1-H]$^-$
Elemental analysis calcd (%) for $C_{15}H_{25}N_5O$: C 61.83, H 8.65, N 24.03; found: C 61.94, H 8.64, N 24.04.

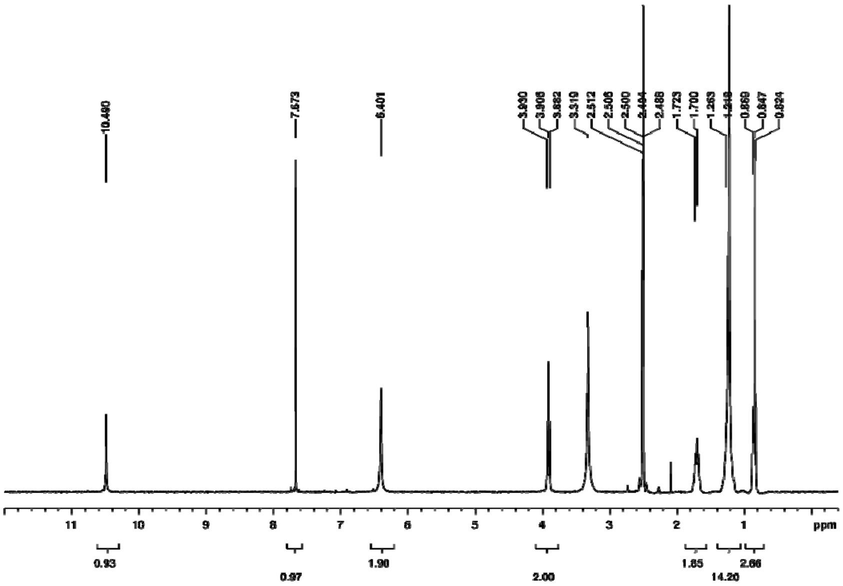


Figure S6:^{1}H-NMR spectrum (400 MHz) of **5** in DMSO-d$_6$

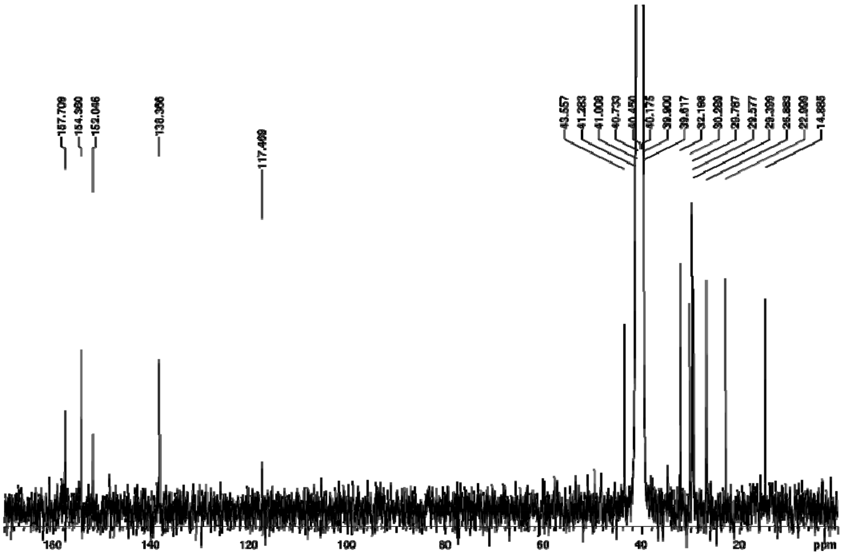


Figure S7:^{13}C-NMR spectrum (400 MHz) of **5** in DMSO

9-Dodecylguanine (6)

The general procedure described above was followed. Petroleum ether/ethyl acetate 1:1 was used for the purification of the protected N-9 dodecyl guanine. Dichloromethane/methanol 94:6 was used for the purification of the title compound. 54 % yield.

ESI-MS: *m/z (%)*: 318.1 (100) [1-H]$^-$
Elemental analysis calcd (%) for $C_{17}H_{29}N_5O$: C 63.92, H 9.15, N 21.92; found: C 63.87, H 9.16, N 21.95.

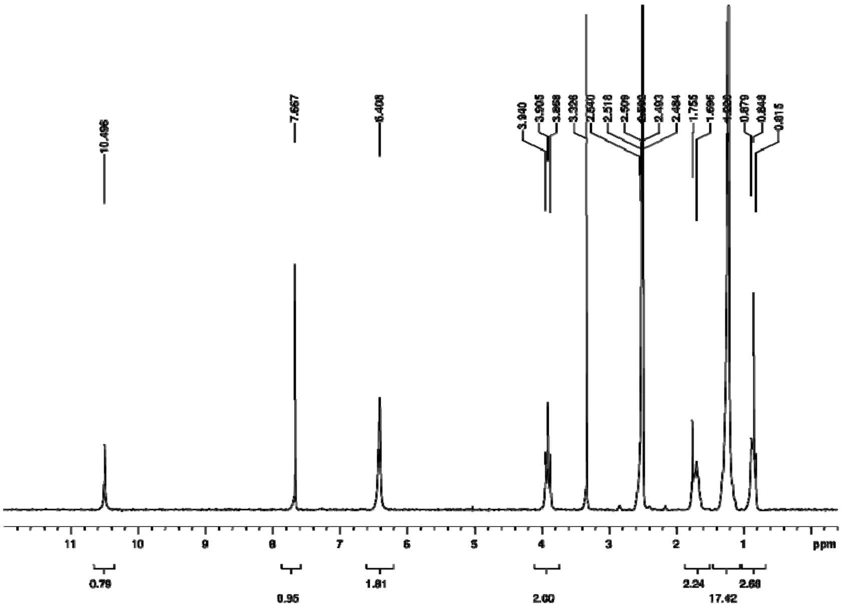


Figure S8: ^{1}H-NMR spectrum (400 MHz) of **6** in DMSO-d_6

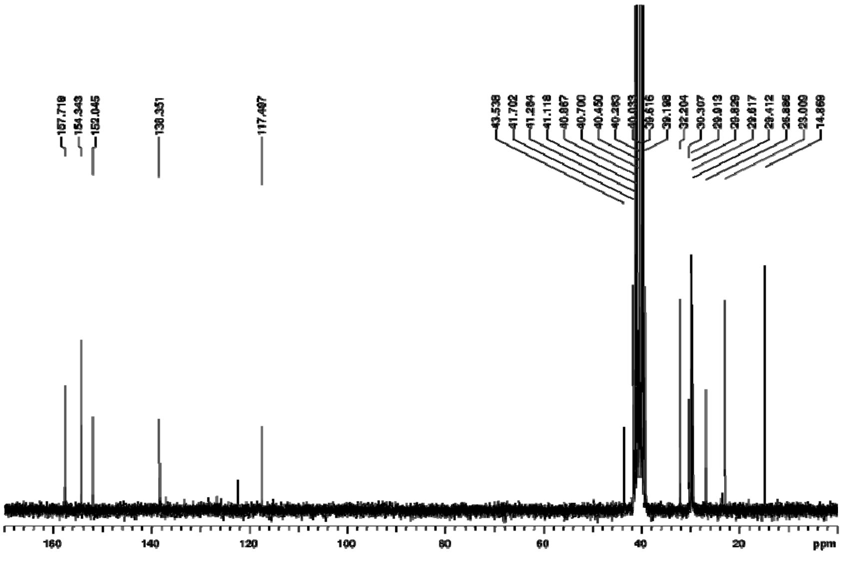


Figure S9: ^{13}C-NMR spectrum (400 MHz) of **6** in DMSO-d_6

9-Tetradecylguanine (7)

The general procedure described above was followed. Petroleum ether/ethyl acetate 1:1 was used for the purification of the protected N-9 tetradecyl guanine. Dichloromethane/methanol 96:4 was used for the purification of the title compound. 20 % yield.

ESI-MS: *m/z (%)*: 346.1 (100) $[1\text{-H}]^-$
Elemental analysis calcd (%) for $C_{19}H_{33}N_5O$: C 65.67, H 9.57, N 20.15; found: C 65.85, H 9.59, N 20.20.

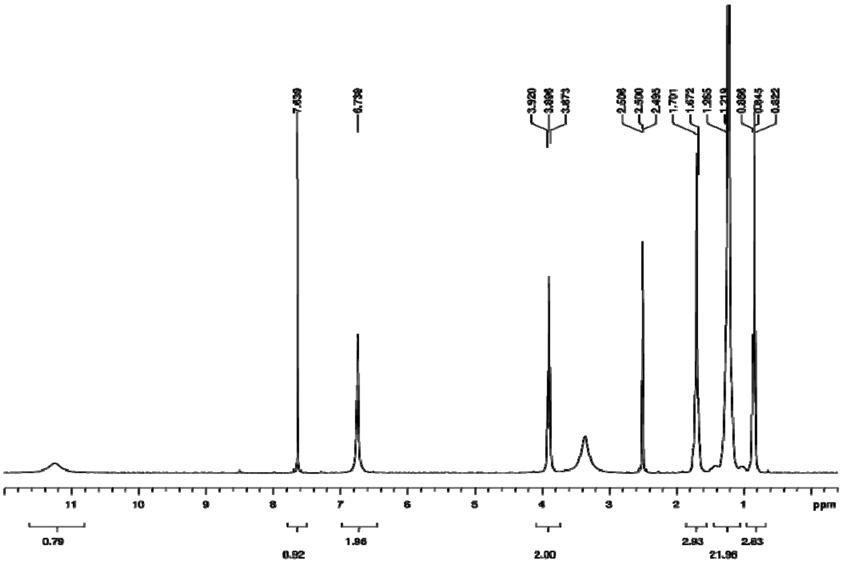


Figure S10: ^{1}H-NMR spectrum (400 MHz) of **7** in DMSO-d_6

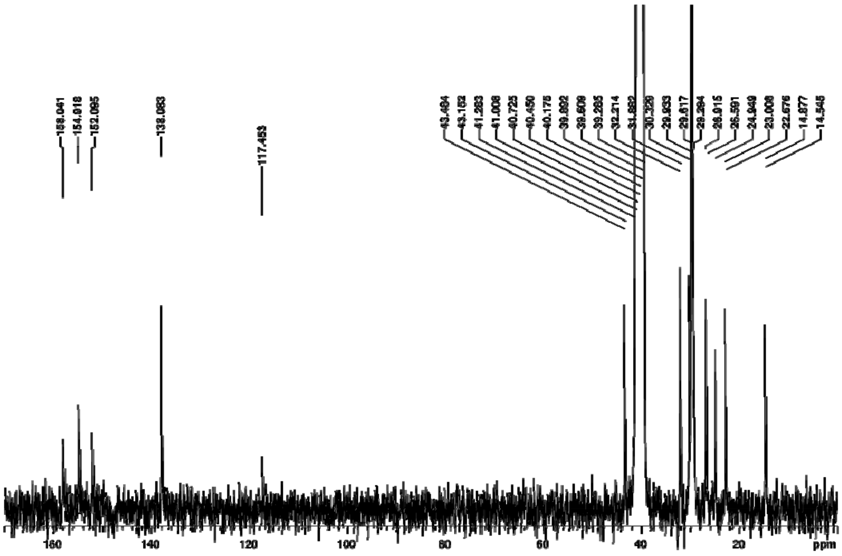


Figure S11: ^{13}C-NMR spectrum (400 MHz) of **7** in DMSO-d_6

9-Hexadecylguanine (8)

The general procedure described above was followed. Petroleum ether/ethyl acetate 1:1 was used for the purification of the protected N-9 hexadecyl guanine. Dichloromethane/methanol 94:6 was used for the purification of the title compound. 26 % yield.

ESI-MS: *m/z (%)*: 374.1 (100) $[1\text{-H}]^-$
Elemental analysis calcd (%) for $C_{21}H_{37}N_5O$: C 67.16, H 9.93, N 18.65; found: C 67.00, H 9.95, N 18.61.

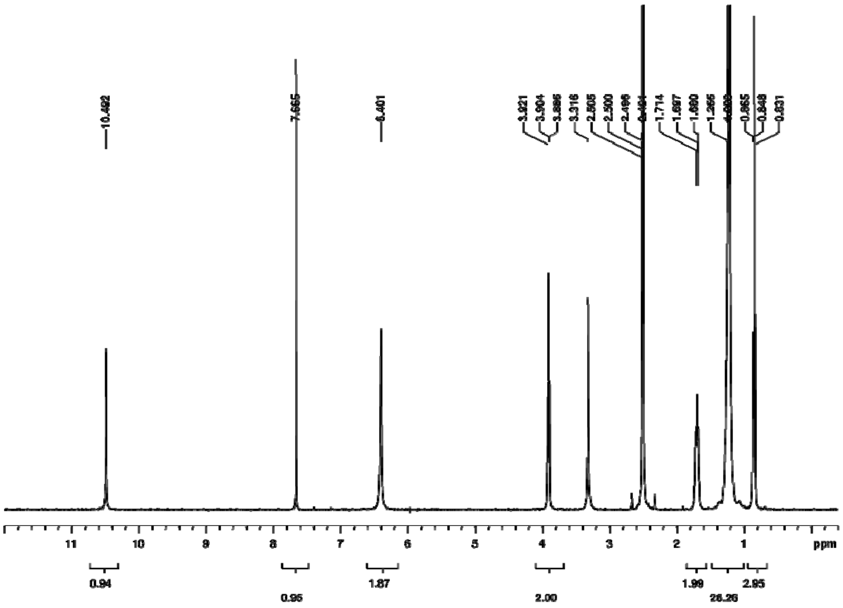


Figure S12: ^{1}H-NMR spectrum (400 MHz) of **8** in DMSO-d_6

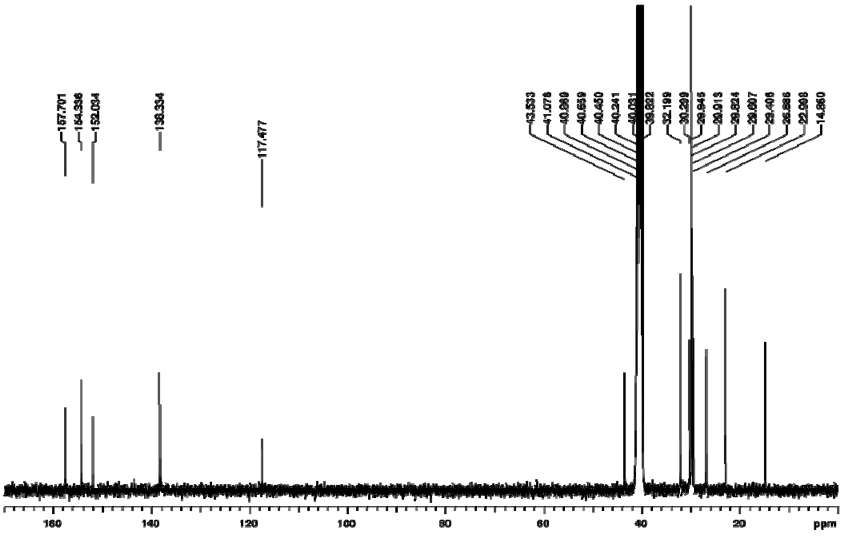


Figure S13: ^{13}C-NMR spectrum (400 MHz) of **8** in DMSO-d_6

2. Investigation in solution by NMR

The solution self-assembly behavior of 9-alkylguanines **1**, **2**, **5** was followed by NMR measured at variable temperatures. 6 mM solutions in the non-competing solvent $C_2D_2Cl_4$ were prepared. For the less soluble derivative **1** the addition of 7% v/v of DMSO-d_6 as a co-solvent was necessary. ^{1}H NMR spectra were recorded in the range 30-90°C: spectra at three selected representative temperatures are reported in figures S14, S15, S16.

For all of the three compounds deshielding of both -NH and –NH_2 signals was observed by lowering temperature, indicating their progressive involvement in hydrogen bonding stabilising ribbon-like architectures (see ref. (S-4)).

These NMR data are similar to those reported for derivative **9** in ref. (S-3).

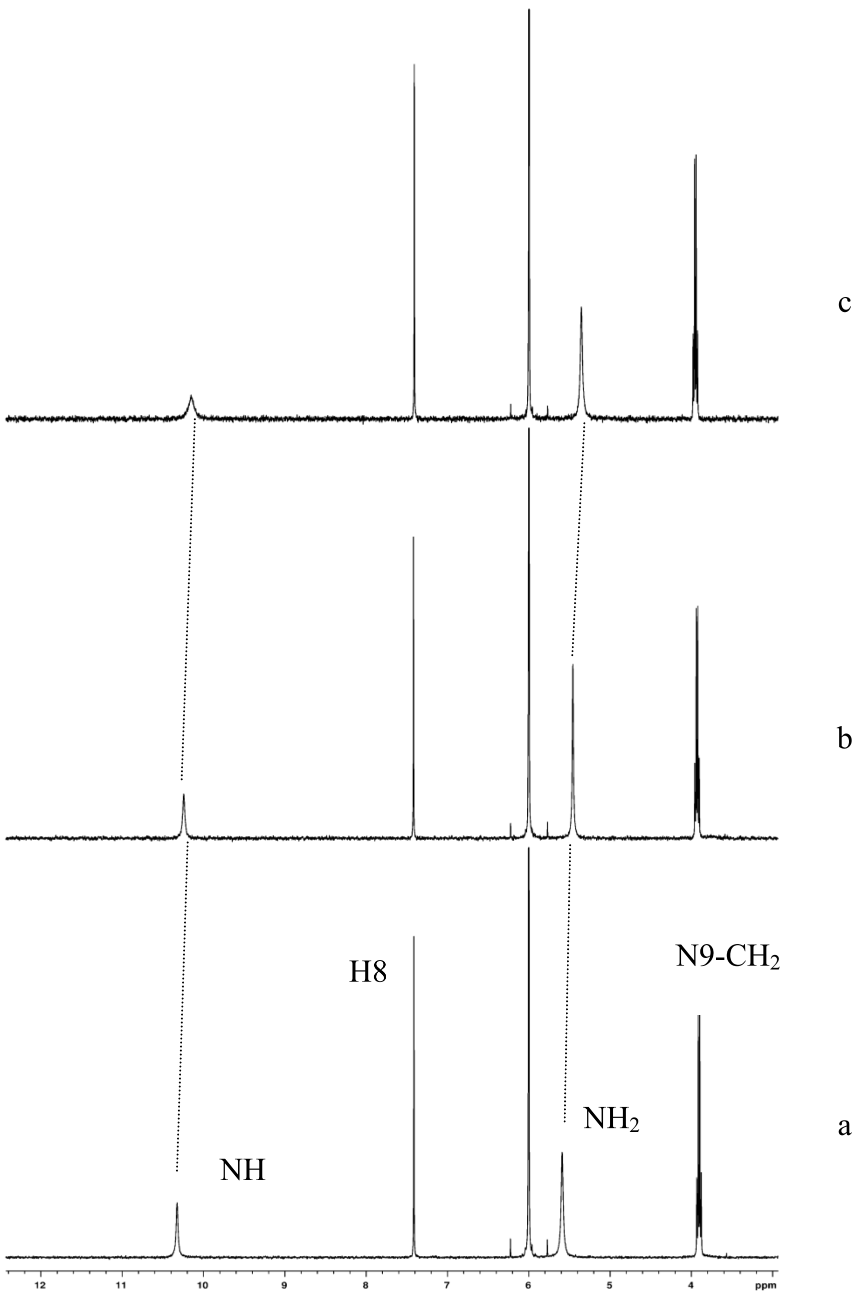
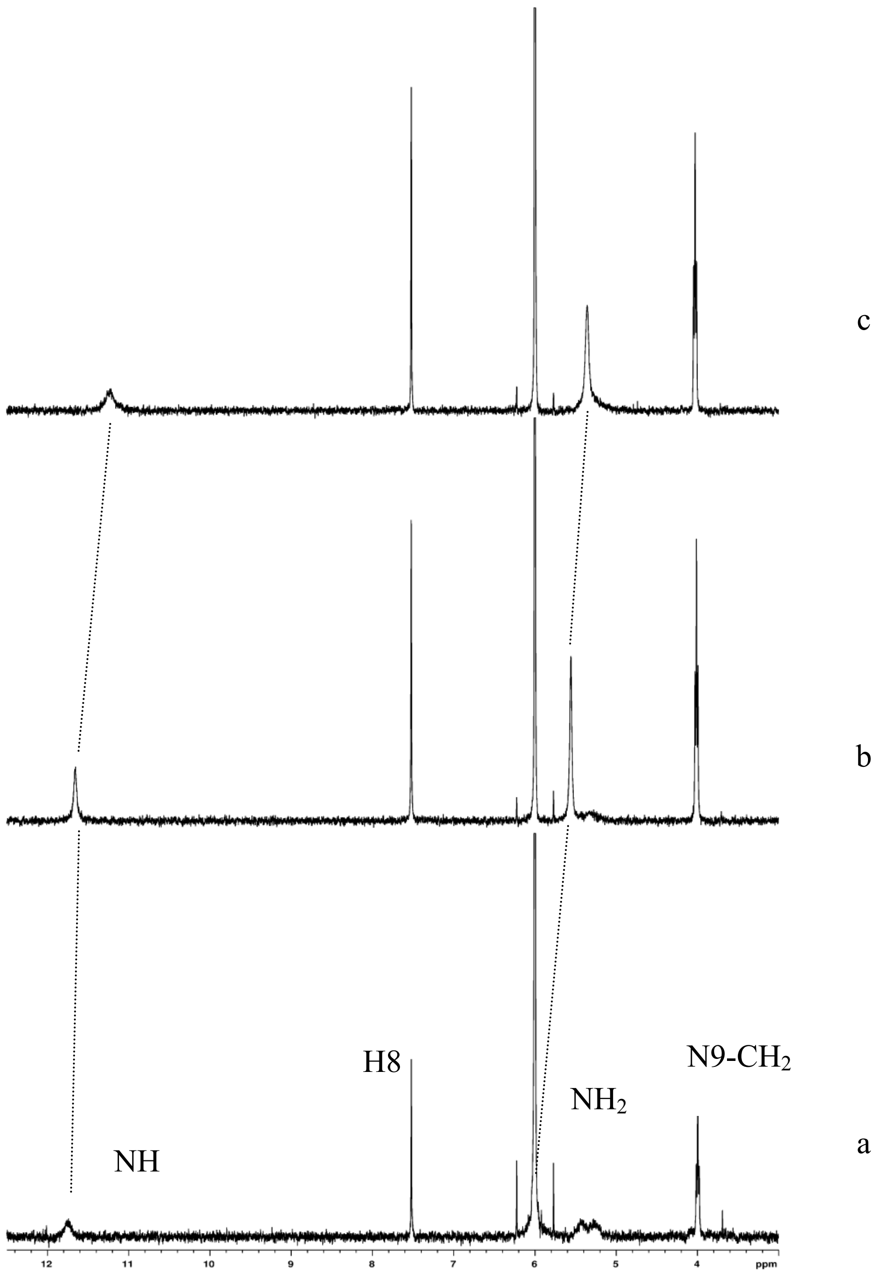


Figure S14: ^{1}H-NMR spectra (600 MHz) of **1** (6 mM in $C_2D_2Cl_4$/DMSO-d_6 93/7) at 30°C (a), 60°C(b), 90°C (c).



FigureS15: ^{1}H-NMR spectra (400 MHz) of **2** (6 mM in $C_2D_2Cl_4$) at 30°C (a), 60°C(b), 90°C (c)

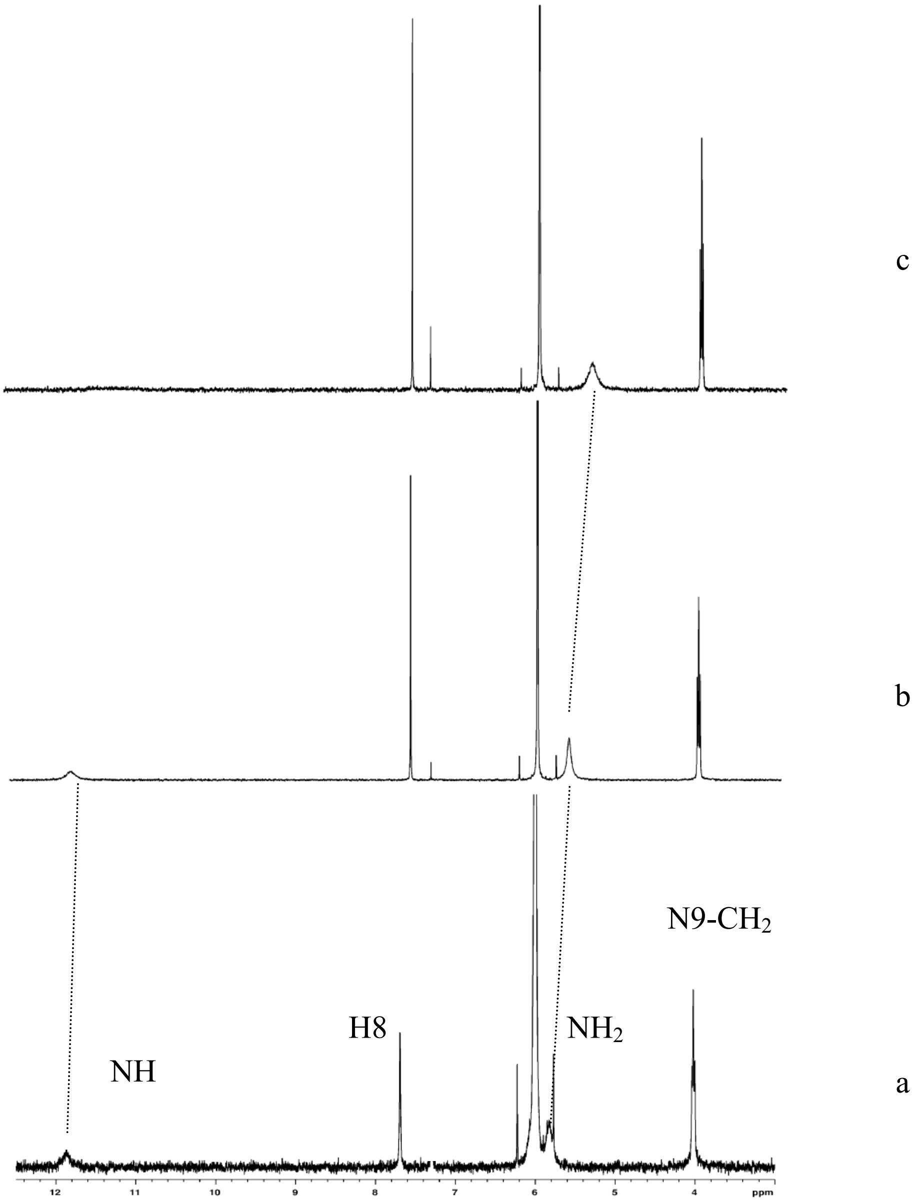


Figure S16: ^{1}H-NMR spectra (400 MHz) of **5** (6 mM in $C_2D_2Cl_4$) at 30°C (a), 60°C(b), 90°C (c)

3. STM investigation

STM measurements were performed using a Veeco scanning tunneling microscope (multimode Nanoscope III, Veeco) in constant current mode at the interface between highly oriented pyrolitic graphite (HOPG) and a supernatant solution. Diluted solutions of all guanine derivatives were applied to the basal plane of the surface. For STM measurements the substrates were glued on a magnetic disk and an electric contact is made with silver paint (Aldrich Chemicals). The STM tips were mechanically cut from a Pt/Ir wire (90/10, diameter 0.25 mm). The raw STM data were processed through the application of background flattening and the drift was corrected using the underlying graphite lattice as a reference. The latter lattice was visualized by lowering the bias voltage to 20 mV and raising the current to 65 pA. All of the models were minimized with Chem3D at the MM2 level, which includes potentials for H-bonds and torsion potentials for describing rotations around single bonds. We decided to use MM2 force filed since is a rather inexpensive method from the computational time viewpoint which has been proven to be successfully employed to describe poly-atomic structures based on H-bonding. Mother solution of alkylated guanine derivatives were dissolved in DMSO at 95ºC and diluted with 1,2,4-trichlorobenzene (TCB) to give 1mM solutions. Monolayer pattern formation was achieved by applying 4μL of solution onto freshly cleaved HOPG. Then STM images were recorded only after achieving a negligible thermal drift.

3.1 Theoretical models

Figures S17-S22 shows the comparison of the proposed molecular packing observed with STM with theoretical models of the guanine derivatives **1**-**9**. In all figures the original STM image was removed in order to make the pictures more clear.

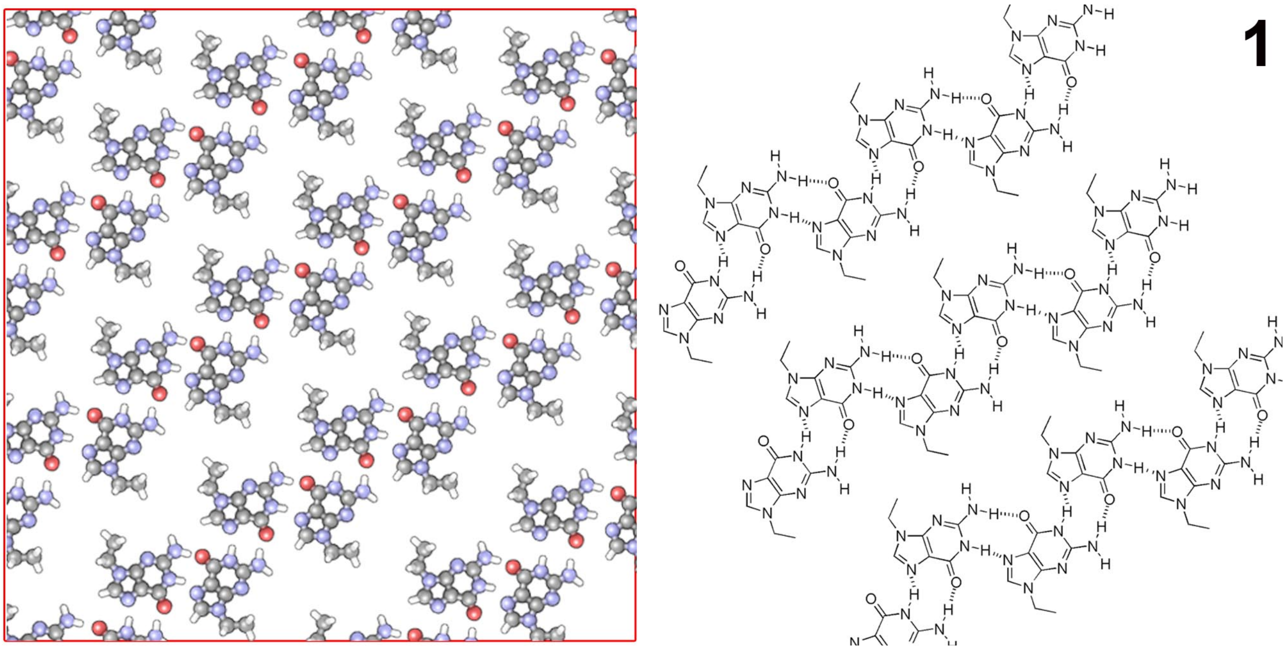


Figure S17: Comparison of the proposed molecular packing of **1** (shown in Fig. 2a in the main text) with theoretical model.

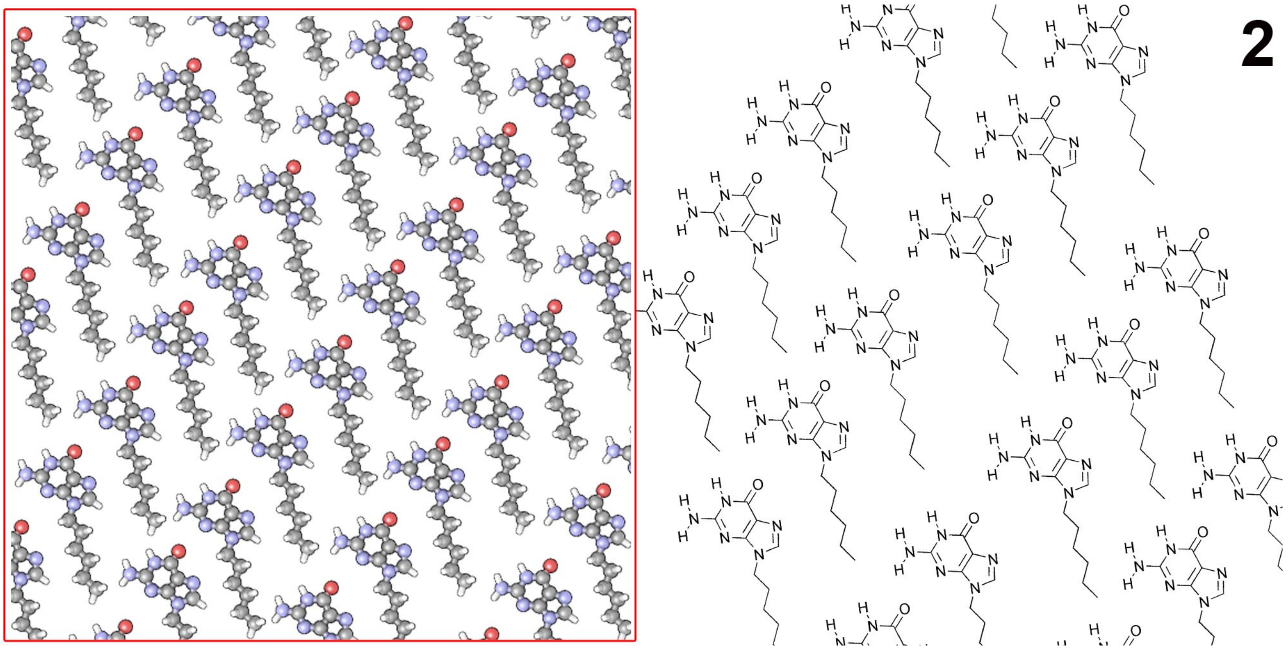


Figure S18: Comparison of the proposed molecular packing of **2** (shown in Fig. 2b in the main text) with theoretical model.

3

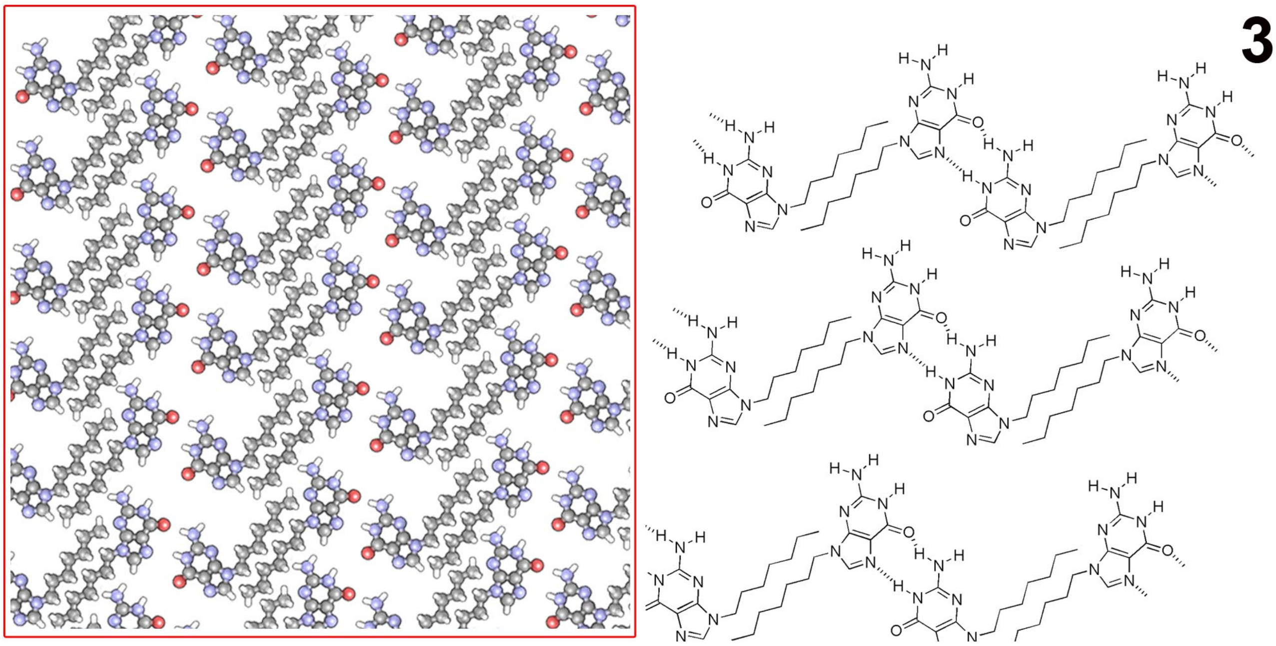


Figure S19: Comparison of the proposed molecular packing of **3** (shown in Fig. 3a in the main text) with theoretical model.

4

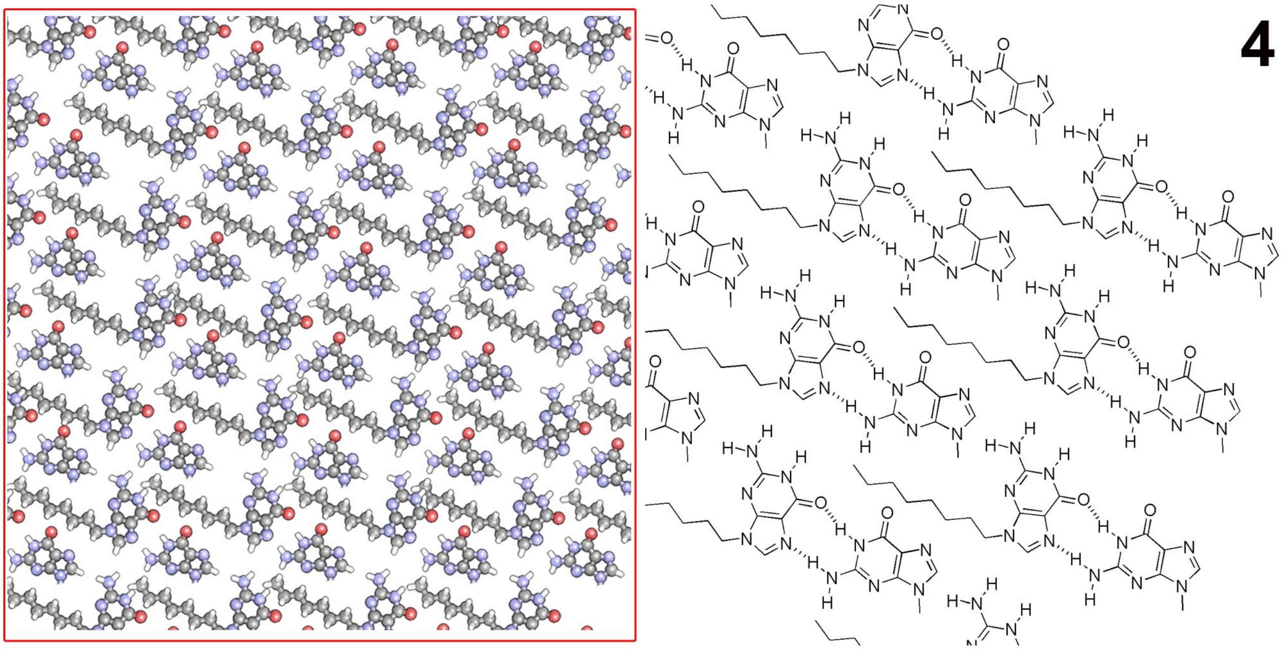


Figure S20: Comparison of the proposed molecular packing of **4** (shown in Fig. 3b in the main text) with theoretical model.

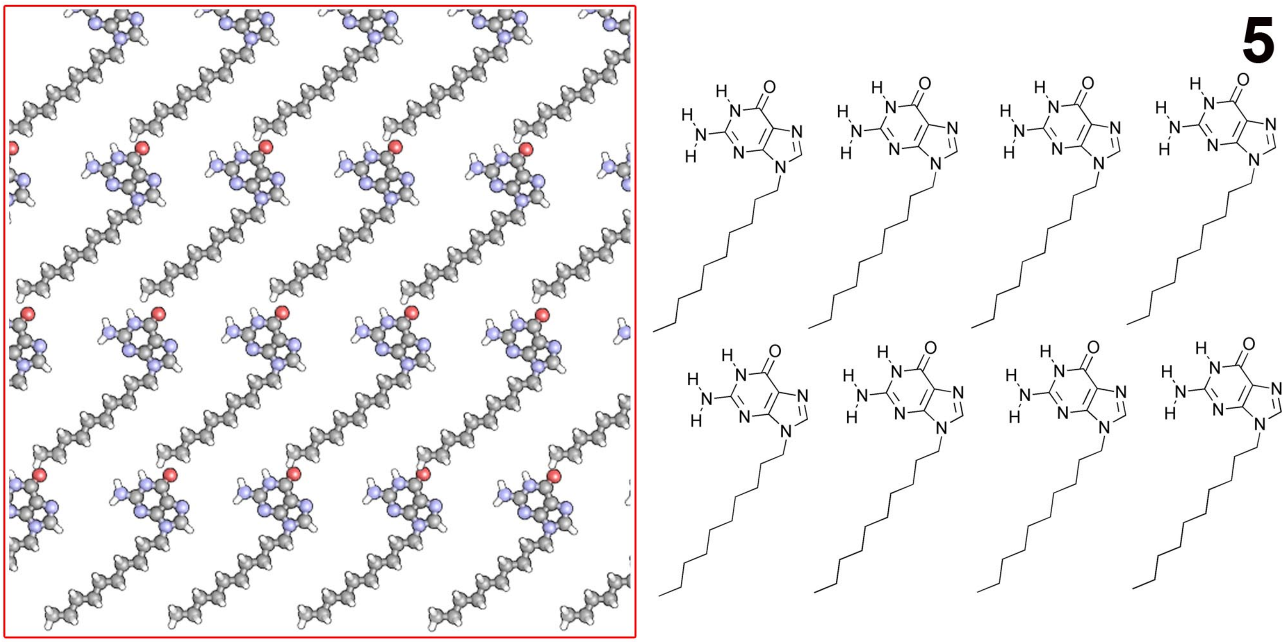


Figure S21: Comparison of the proposed molecular packing of **5** (shown in Fig. 2c in the main text) with theoretical model.

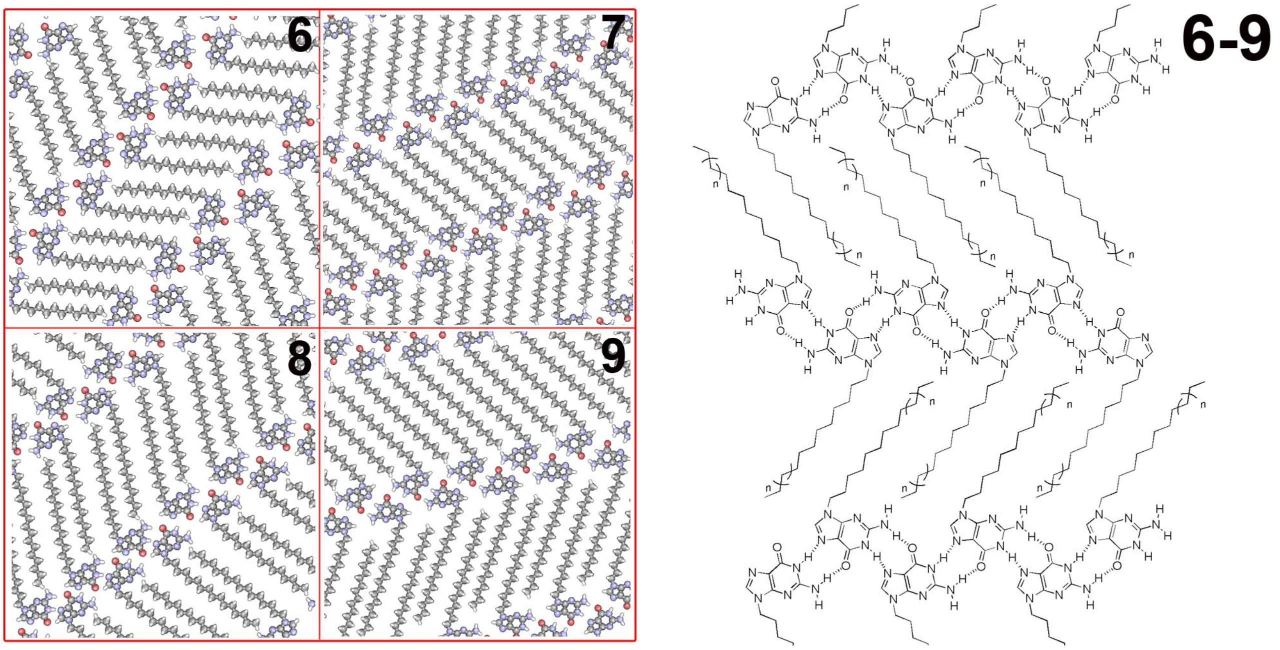


Figure S22: Comparison of the proposed molecular packing of molecules **6-9** (shown in Fig. 4 in the main text) with corresponding theoretical model (n = 1,2,4,6).

3.2 Energy of physisorption of alkyl chains on HOPG surface

Table S1: Energy of physisorption of alkyl chains with increasing length on HOPG surface

Guanine derivative	Side chain	Adsorption energy in kcal/mol*
1	C_2H_5	5.2
2	C_6H_{13}	15.6
3	C_7H_{15}	18.2
4	C_8H_{17}	20.8
5	$C_{10}H_{21}$	26
6	$C_{12}H_{25}$	31.2
7	$C_{14}H_{29}$	36.4
8	$C_{16}H_{33}$	41.6
9	$C_{18}H_{37}$	46.8

*The adsorption energy of alkyl chains on the HOPG surface

Note that the adsorption energy of one methylene group on graphite is around 2.6 kcal/mol (11 kJ/mol, ~0.1 eV). (S-5) Therefore, the adsorption energy of guanine derivatives **1-9** was estimated by multiplying this value by the number of methylene units in the alkyl chains of adjacent guanine derivatives.

References

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