Electronic supplementary information (ESI)

Nanopatterning the graphite surface with ordered macrocyclic or ribbon-like assemblies of isocytosine derivatives: an STM study

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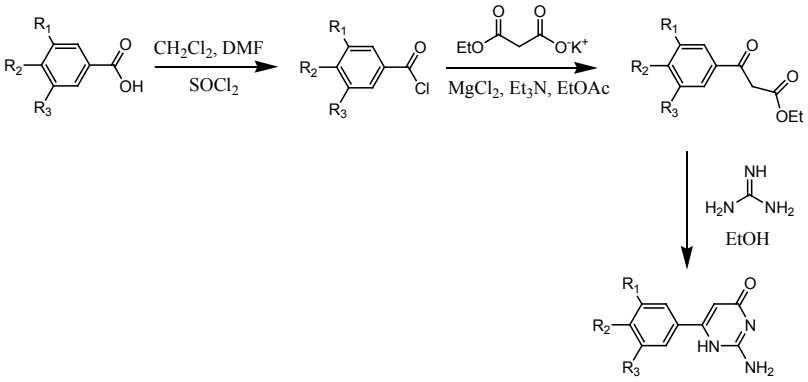
1. Experimental Procedures:

General methods

All reagents were analytical grade and used as received. The solvents were carefully dried and freshly distilled prior to use according to common laboratory practice. All reactions were performed under dry Argon atmosphere using standard Schlenk techniques. Flash chromatography was performed with silica gel 60 (particle size 63 – 200 μm, 230 – 400 mesh, Merck®). ^{1}H NMR spectra were recorded at 295 K using a Bruker Avance 400 spectrometer at 400 MHz. The chemical shifts (δ) are given in ppm and the residual solvent peak was used as reference for calibration. Peaks are described as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m).

Synthesis

6-[4-(octyloxy) phenyl]isocytosine (**1**) and 6-[3,4,5-(triethoxy)phenyl]isocytosine (**2**) were synthesized by ring closure of the corresponding β-keto ester with guanidine carbonate, as reported by E. W. Meijer et al.[1]



Scheme S1. Synthesis of compounds **1** and **2**.

*Synthesis of **1***

4-(octyloxy) benzoyl chloride: 4-(octyloxy) benzoic acid (5g, 0.02 mol) was dissolved in dichloromethane with few drops of DMF as catalyst for the reaction. Thionyl chloride (2.4 g, 0.02 mol) was slowly added at the reaction mixture which was stirred at room temperature for 2 hours. The reaction mixture was evaporated, and the acid chloride was used without any further purification.

Ethyl 4-(octyloxy) benzoyl acetate: In a 300 mL three-necked round bottom flask a suspension of potassium ethyl malonate (4.3 g, 0.026 mol) and triethylamine (8.1g, 11 mL) in 50 mL of ethyl acetate was charged and cooled down in an ice bath. Dry $MgCl_2$ (3.4 g, 0.036 mol) was added slowly. The mixture was heated to 40°C and stirred at that temperature overnight. After that time, the temperature was decreased to 0°C again and 4-(octyloxy) benzoyl chloride synthesized in the previous step was added dropwise to the potassium malonate suspension.The reaction mixture was allowed to worm to room temperature and stirred overnight. After that it was cooled down in an ice bath followed by careful addition of aqueous hydrochloric acid (12%, 25 mL). The organic layer was extracted with toluene, the extract was then washed with aqueous hydrochloric acid (12%), with a 5% aqueous solution of sodium bicarbonate and dried over $MgSO_4$. The organic layer was collected and the solvent was evaporated *in vacuo* to afford the crude title compound, which was used in the next step without further purification (5.06g, 79%). ^{1}H-NMR (CDCl3, δ): 7.92 (d, 2H, J = 8.8Hz), 6.93 (d, 2H, J = 8.8Hz), 4.22 (q, 2H, J = 7. 2Hz), 4.03 (t, 2H, J = 6.8Hz), 3.95 (s, 2H), 1.81 (m, 2H), 1.47 (m, 3H), 1.35 – 1.25 (m, 10H), 0.90 (m, 3H).

*6-[4-(octyloxy)phenyl] isocytosine (**1**)*: A 300 mL three-necked round bottom flask was charged with a suspension of ethyl 4-(octyloxy) benzoyl acetate (5.06g, 0.0158 mol) and guanidine carbonate (3.93g, 0.0163 mol) in 50 mL of absolute ethanol. The reaction mixture was refluxed overnight, then the solvent was removed in vacuo. The residue was extracted with ethyl acetate and water. The organic layer was collected, dried over $MgSO_4$ and evaporated. The crude product was washed with chloroform to give the title compound as a white solid in a 51 % yield (2.5 g). ^{1}H-NMR (DMSO, δ): 10.70 (s, 1H), 7.90 (d, 2H, J = 8.0Hz), 6.96 (d, 2H, J = 8.0Hz), 6.54 (s, broad, 2H), 6.03 (s, 1H), 4.01 (m, 2H), 1.73 (m, 2H), 1.50 – 1.19 (m, 10H), 0.87 (m, 3H).

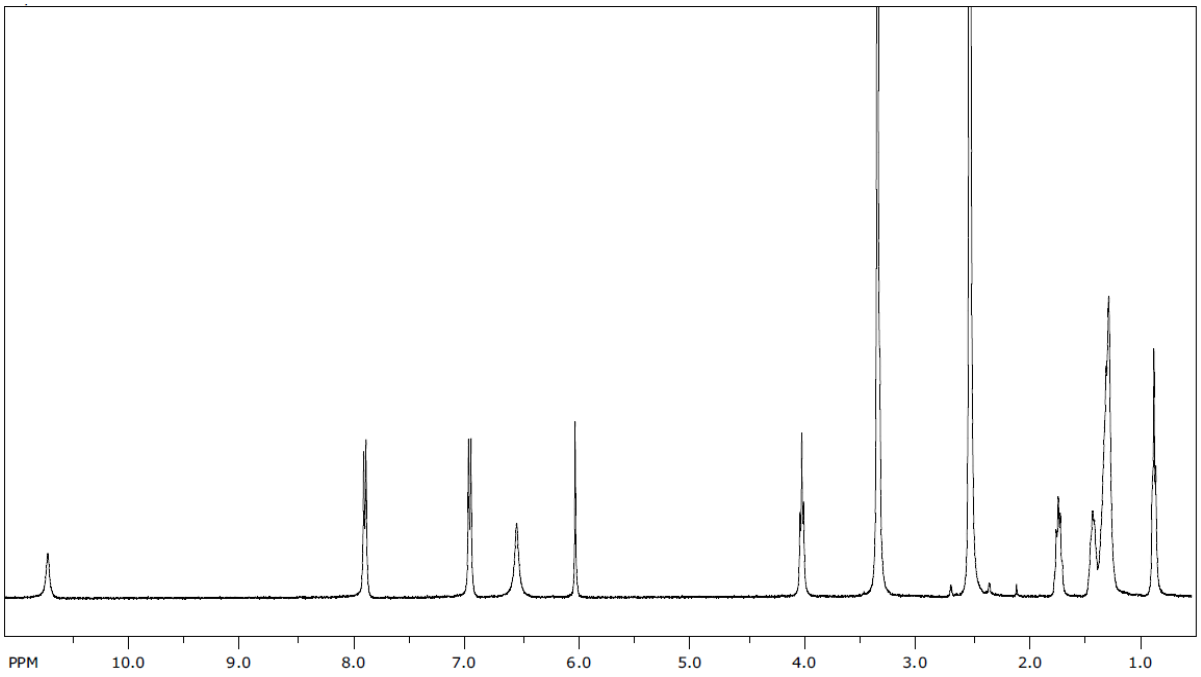


Figure S1. ^{1}H NMR spectrum of **1** ([D_6]DMSO, 400 MHz).

*Synthesis of **2***

The adopted synthetic route for *ethyl 3,4,5-(triethoxy) benzoyl acetate* was the same reported for ethyl 4-(octyloxy) benzoyl acetate.

6-[3,4,5-(triethoxy)phenyl]isocytosine (2): A 300 mL three-necked round bottom flask was charged with a suspension of ethyl 3,4,5-(triethoxy) benzoyl acetate (5g, 0.0154 mol) and guanidine carbonate (3.93g, 0.0163 mol) in 50 mL of absolute ethanol. The reaction mixture was refluxed overnight, then the solvent was removed in vacuo. The residue was dissolved in chloroform and extracted with water and saturated NaCl solution. The organic layer was collected, dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography using a gradient mobile phase from pure chloroform to 10 vol% of methanol in chloroform to afford the title compound in a 39 % yield (1.9g). ^{1}H-NMR (DMSO, δ): 10.75 (s, 1H), 7.22 (s, 2H), 6.56 (s broad, 2H), 6.15 (s, 1H), 4.09 (q, 4H, J = 6.8Hz), 3.99 (q, 2H, J = 6.8Hz), 1.35 (t, 6H, J = 6.8Hz), 1.25 (t, 3H, J = 6.8Hz).

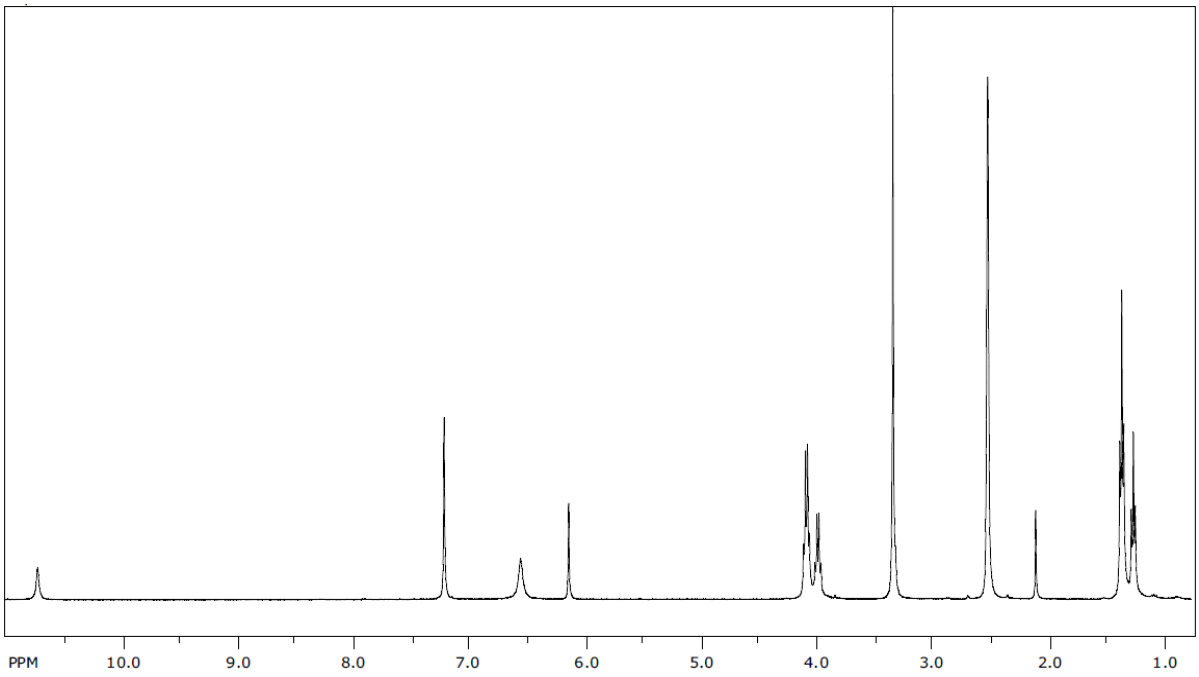


Figure S2. ^{1}H NMR spectrum of **2** ([D_6]DMSO, 400 MHz).

2. Self-assembly of isocytosine derivatives:

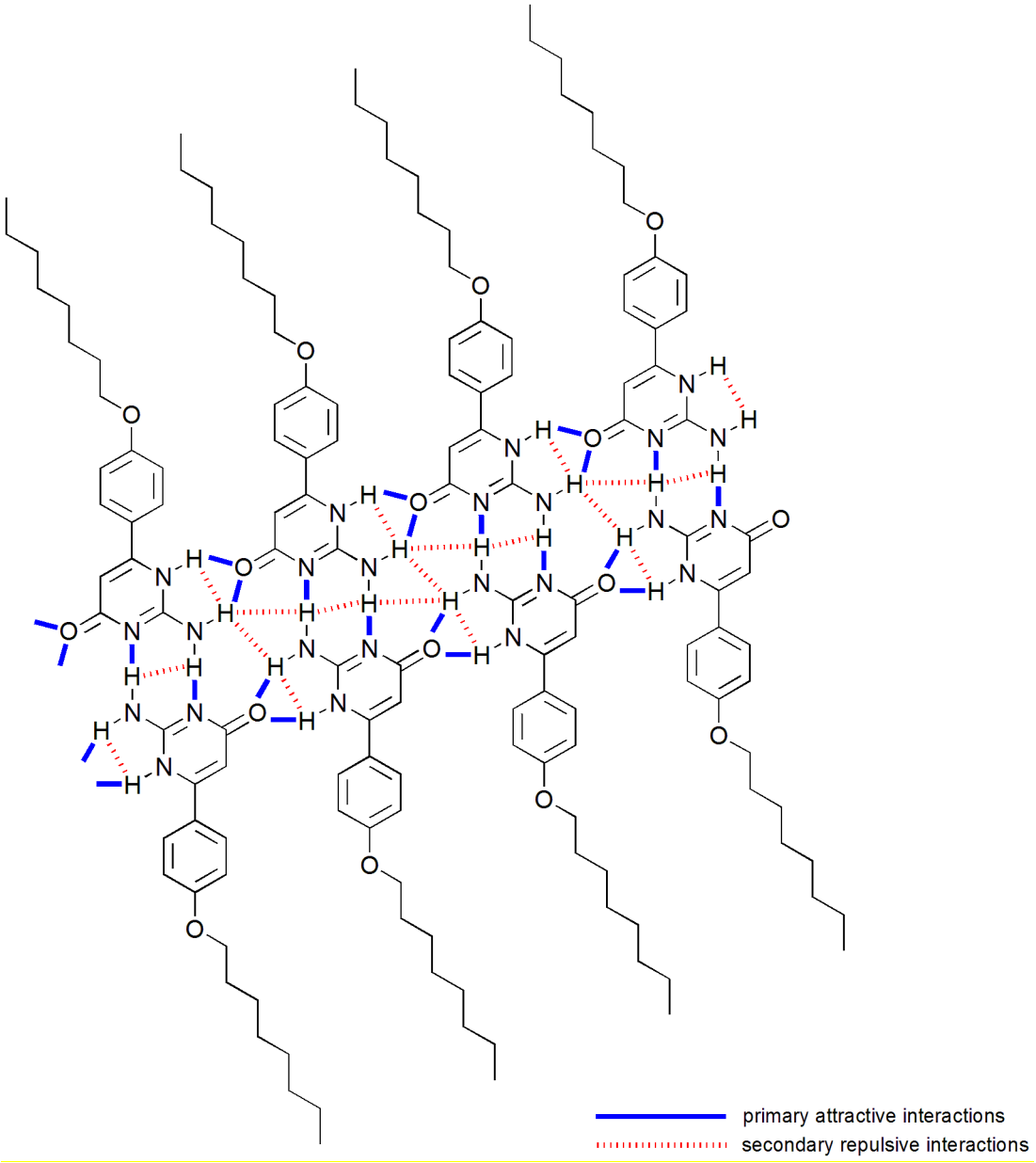


Figure S3. The supramolecular 1D hydrogen-bonded ribbon formed by **1** at the solid-liquid interface. Primary attractive and senondary repulsive interactions are indicated in blue and red, respectively.

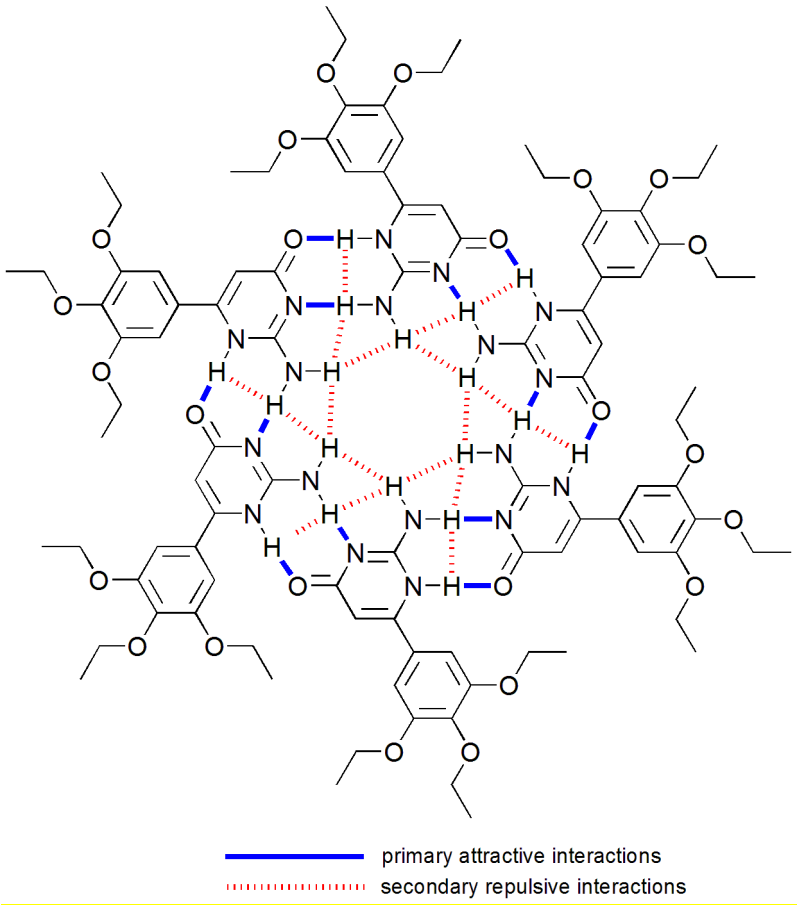


Figure S4. Macrocyclic hydrogen-bonded hexameric motif, formed by molecules **2** at the solid-liquid interface. Primary attractive and senondary repulsive interactions are indicated in blue and red, respectively.

3. STM investigation

Scanning Tunneling Microscopy (STM) measurements were performed using a Veeco scanning tunneling microscope (multimode Nanoscope III, Veeco) at the interface between highly oriented pyrolitic graphite (HOPG) and a supernatant solution, by using a scanner A (Veeco), therefore by mapping an area of 1µm × 1µm. Diluted solutions of **1** 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. Mother solution of 6-[4-(octyloxy) phenyl]isocytosine (**1**) and 6-[3,4,5-(triethoxy)phenyl]isocytosine (**2**) were dissolved in 1,2,4-trichlorobenzene at 95ºC and diluted to give 400 µM, 40 µM and 4 µM solutions. STM imaging was carried out in constant height mode yet without turning off the

feedback loop, to avoid tip crashes. Monolayer pattern formation was achieved by applying onto freshly cleaved HOPG a 4μL of a solution that was heated at warm 60-70ºC to improve the solubility. The STM images were recorded only after achieving a negligible thermal drift. By using lower temperature during the heating process, small precipitating agglomerates were observed. On the other hand, in-situ STM experiments at variable temperature cannot be performed using our set-up. All of the molecular models were minimized with Chem3D at the MM2 level and processed with QuteMol visualization software.[2]

4. References

1. a) F. H. Beijer, R. P. Sijbesma, H. Kooijman, A. L. Spek and E. W. Meijer, *J. Am. Chem. Soc.*, 1998, **120**, 6761-6769; b) J. H. K. K. Hirschberg, R. A. Koevoets, R. P. Sijbesma and E. W. Meijer, *Chem. Eur. J.*, 2003, **9**, 4222-4231.
2. M. Tarini, P. Cignoni and C. Montani, *IEEE T. Vis. Comput. Gr.*, 2006, **12**, 1237-1244.