Ordered Honeycomb Microporous Films from Self-assembly of Alkylated Guanosine Derivatives

Supporting Information

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CONTENTS

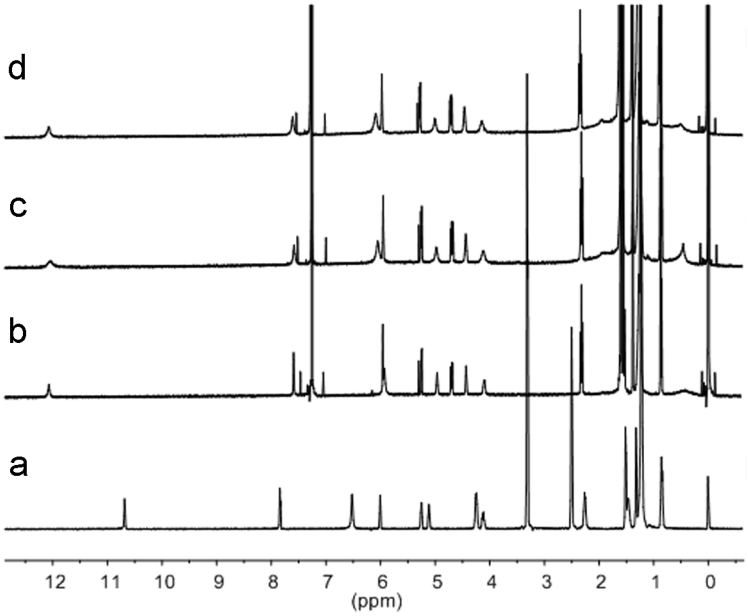


Figure S1. ^{1}H NMR spectra of **1** at 298 K of (a) 10 mM in DMSO-d_6 and (b) 1.0, (c) 2.5, and (d) 10 mM in $CDCl_3$.

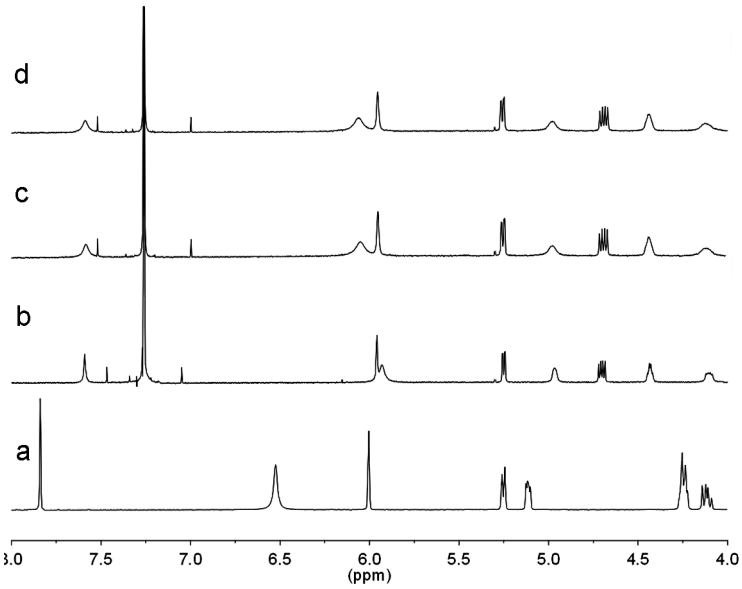


Figure S2. Portion of ^{1}H NMR spectra of **1** over 4.0-8.0 ppm at concentration of (a) 10 mM in DMSO-d_6 and (b) 1.0, (c) 2.5, and (d) 10 mM in $CDCl_3$ at 298 K.

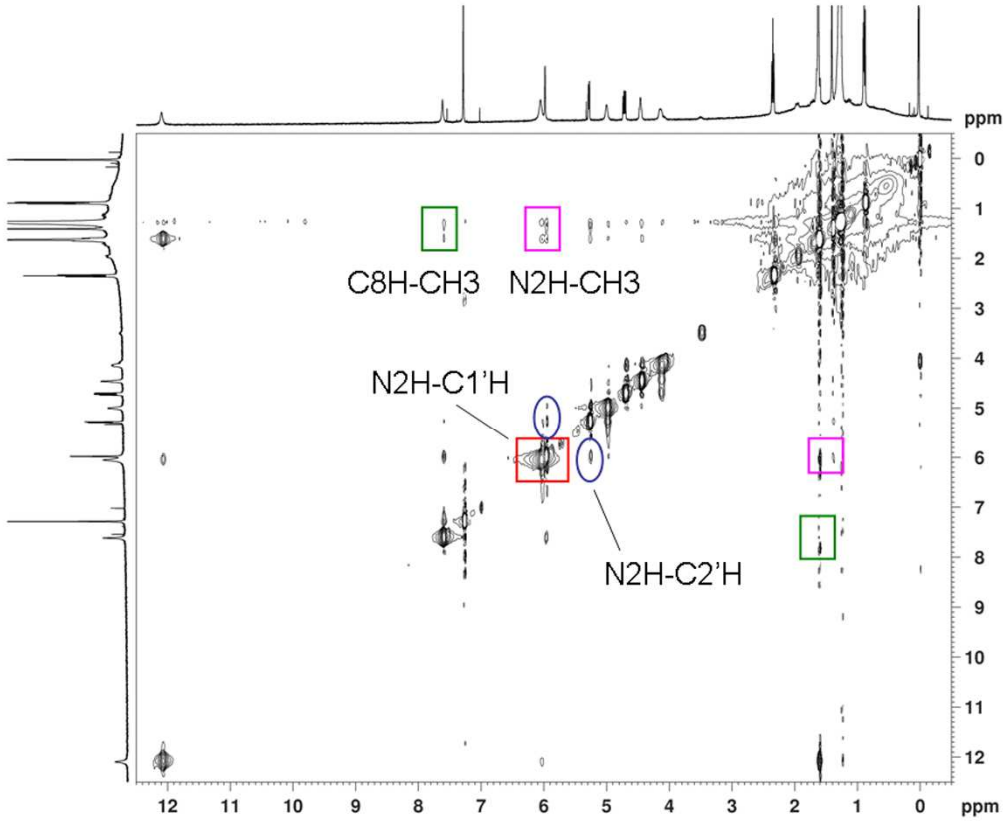


Figure S3. NOESY spectrum of 10 mM **1** in $CDCl_3$ at 298 K.

Diffusion NMR experiments

Diffusion experiments were carried out with a Bruker AV400 spectrometer, the temperature was actively controlled at 25.0 ± 0.5 °C. Diffusion coefficients were derived using integration of the desired peaks to a single exponential decay, using the T1/T2 Relaxation (Bruker TopSpin v 2.0), according to the equation:

$I = I_0 \cdot \exp(-D \cdot (2\pi \cdot \gamma \cdot g \cdot \delta)^2 \cdot (\Delta - \delta/3))$

where I denotes the NMR signal intensity, g is the gradient strength, δ is the gradient pulse duration, Δ is the gradient separation time, γ is the gyromagnetic ration of the nucleus being observed.[1] Experiments consisted 16 points, and each point comprised 256 scans with δ value of 3.6 ms, Δ value of 99.9 ms, and γ value of 4258 Hz per G.

Calculation of the hydrodynamic radii in DMSO-d_6 was performed using the viscosity value ($\eta = 2.0 \times 10^{-3}$ Kg m^{-1} s^{-1}, 298.15 K) provided by the solvent supplier,

in $CDCl_3$ the viscosity value used was ($\eta = 0.54 \times 10^{-3}$ Kg m^{-1} s^{-1}, 298.15 K). The hydrodynamic radii (r_H) were calculated according to the spherical approximation using the Einstein-Stokes equation:

$D = k_B \cdot T / (6\pi \cdot \eta \cdot r_H)$

where T denotes the temperature, η is the viscosity of the solvent at the given temperature and k_B is the Boltzmann-Constant.[1] All the measurements were performed in triplicate and the uncertainty is given by the standard deviation.

Table S1 Diffusion coefficients (D_s) and hydrodynamic radii (r_H) of the monomer and assemblies formed by **1, 2,** and **3** determined by PFG–NMR in DMSO-d_6 and $CDCl_3$.

		1	**2**	**3**
DMSO-d_6[a] 2.5 mM	D_s (10^{-10} m^2/s)	1.92 ± 0.01	2.04 ± 0.03	1.70 ± 0.02
	r_H (Å)	5.68 ± 0.03	5.35 ± 0.08	6.42 ± 0.08
$CDCl_3$[b] 1.0 mM	D_s (10^{-10} m^2/s)	4.73 ± 0.02		
	r_H (Å)	8.54 ± 0.04		
$CDCl_3$[c] 10 mM	D_s (10^{-10} m^2/s)	4.29 ± 0.03	4.33 ± 0.03	3.64 ± 0.05
	r_H (Å)	9.42 ± 0.07	9.33 ± 0.06	11.10 ± 0.15

(a) D_s values were obtained by the analysis of N2-H signals of **1**, **2**, and **3** at 6.53, 6.54, and 6.54 ppm, respectively. (b) D_s value was obtained by the analysis of C1'-H signals of **1** at 5.96 ppm. (c) D_s values were obtained by the analysis of C1'-H signals of **1**, **2**, and **3** at 5.96, 5.95, and 5.95 ppm, respectively

Reference:

[1] (a) Y. Cohen, L. Avram, L. Frish, *Angew. Chem. Int. Ed.* 2005, **44**, 520–554; (b) M. S. Kaucher, Y. F. Lam, S. Pieraccini, G. Gottarelli, J. T. Davis, *Chem. Eur. J.* 2004, **11**, 164–173.

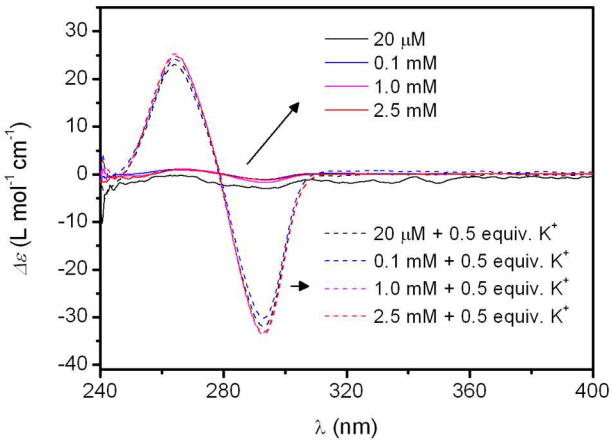


Figure S4. CD spectra of **1** in $CHCl_3$ (solid lines) at 20 μM, 0.1 mM, 1.0 mM and 2.5 mM, respectively in the absence (solid lines) and presence (dashed line) of 0.5 equiv K^+.

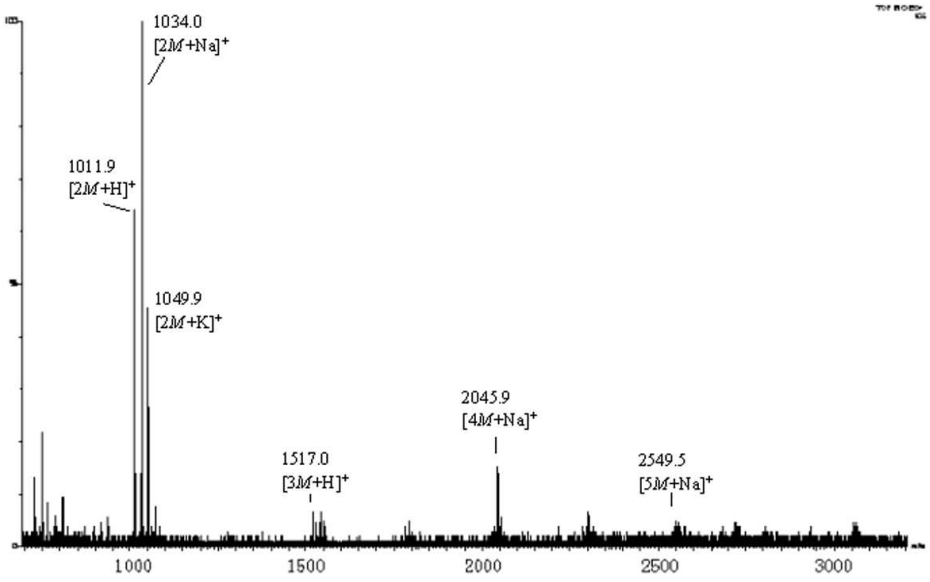


Figure S5. ESI-MS of **1** in $CHCl_3$.

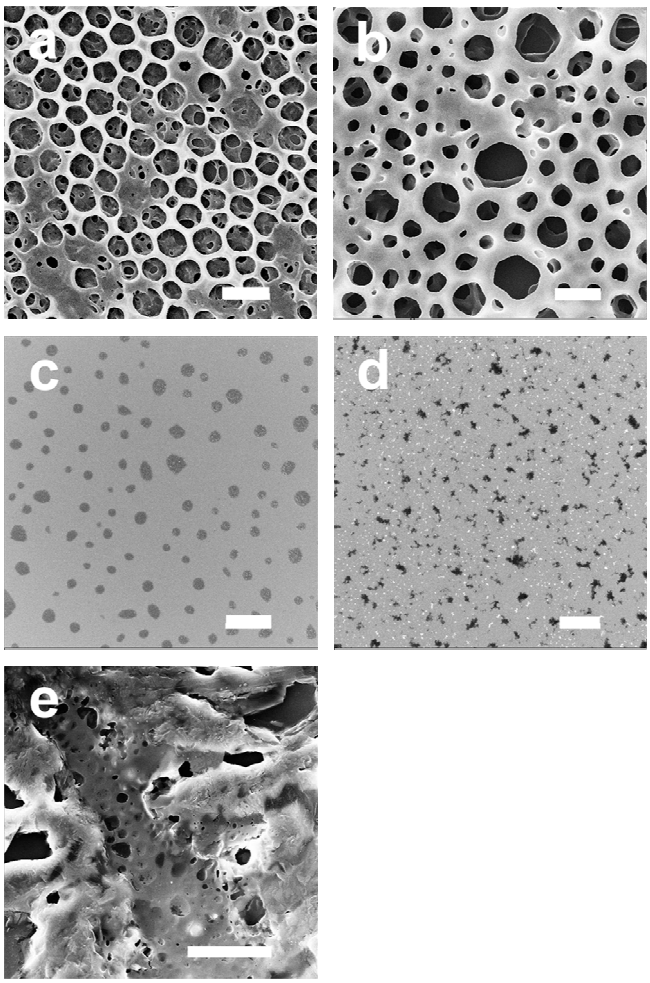


Figure S6. SEM images of films made from different molecules in $CHCl_3$ at 80 ºC: (a) **2** (1.0 mM), (b) **3** (1.0 mM), (c) **4** (1.0 mM), (d) the mixture of **1** (0.5 mM) and **4** (0.5 mM), (e) **1** (0.5 mM) and 0.25 equiv KSCN. The scale bars are 2 μm (a, b), 20 μm (c, e), 10 μm (d), respectively.

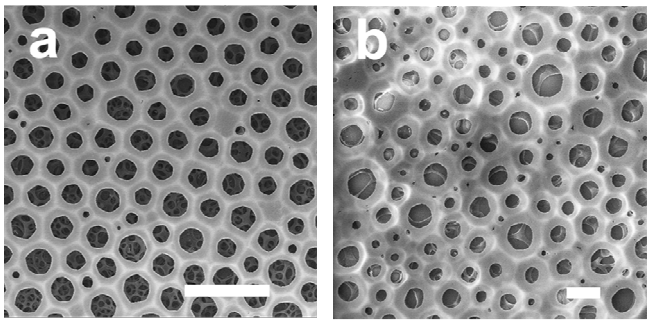


Figure S7. SEM images of honeycomb films made from 0.5 mM **1** in $CHCl_3$ at 80 ºC on (a) gold-coated silicon and (b) glass. The scale bars are 10 (a) and 2 μm (b), respectively.

Modification of silicon surface

Modification of silicon surface was accorded to reference 2, 3. The used n-type Si (100) wafers were cleaned previously using acetone, ethanol, and deionized water three times, respectively. The cleaned Si wafers were oxidized by O_2-plasma to make the surface more hydrophilic.[2,3] Then the oxidized Si wafers were coating with fluoroalkylsilane compound (**F_{13}-OMCS**, Figure S8, Aldrich product) by chemical vapour deposition (CVD) method to make the surface hydrophobic.[2,3] The contact angles of the modified silicon surface were showed in Figure S9.

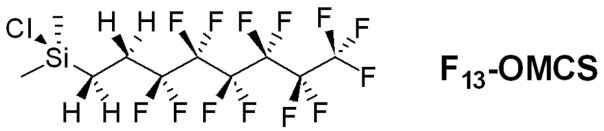


Figure S8. Molecular structure of **F_{13}-OMCS**.

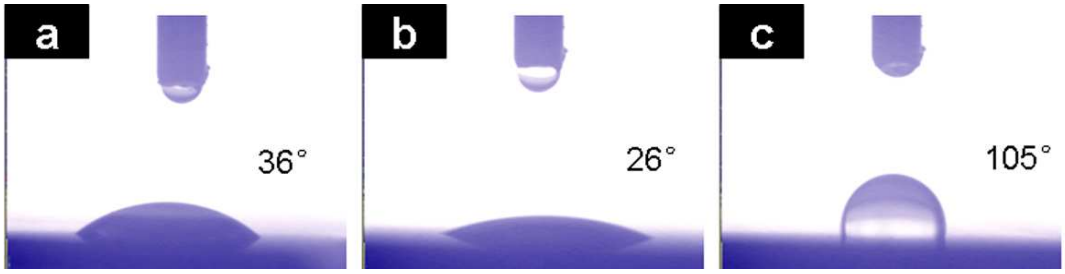


Figure S9. Photographs of water droplets on the different silicon surface: (a) cleaned Si wafer, (b) O_2-plasma treated Si wafer, (c) fluoroalkylsilane coated Si wafer.

References:

[2] A. Hozumi, K. Ushiyama, H. Sugimura, O. Takai, *Langmuir* 1999, **15**, 7600-7604.
[3] H. Schift, S. Saxer, S. Park, C. Padeste, J. Gobrecht, *Nanotechnology* 2005, **16**, S171-S175.

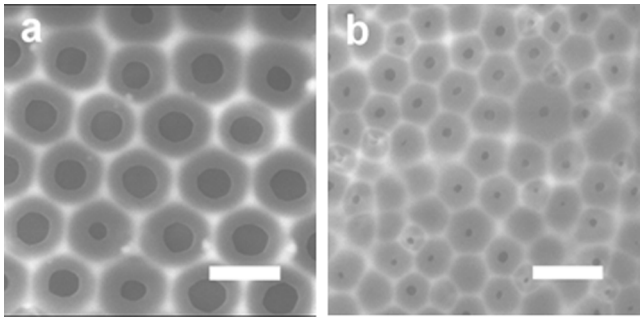


Figure S10. SEM images of honeycomb films made from 0.5 mM **1** in $CHCl_3$ at 80 ºC on (a) O_2-plasma treated silicon and (b) fluoroalkylsilane coated silicon. The scale bars are 2 (a) and 5 μm (b), respectively.

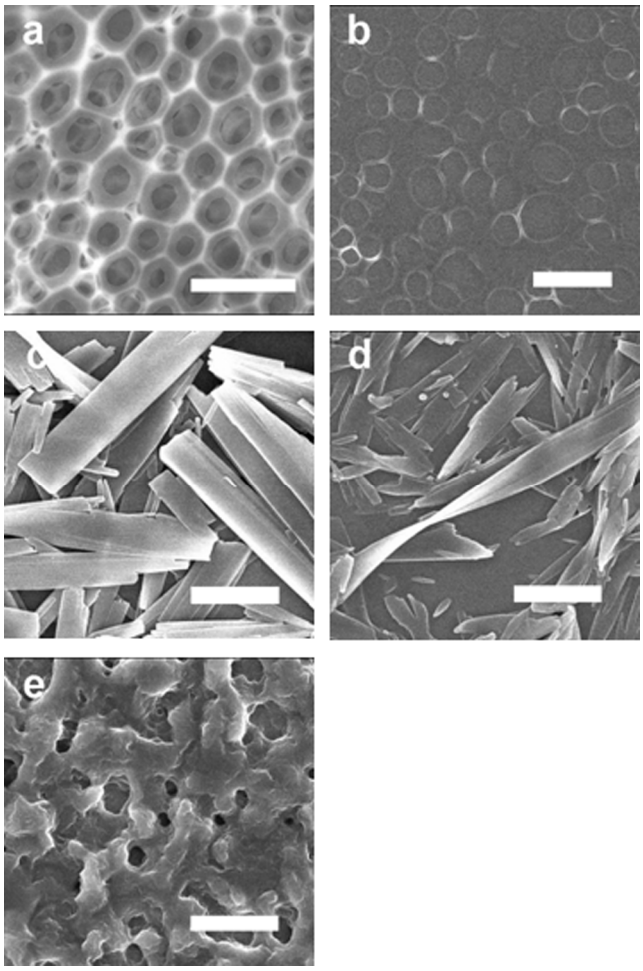


Figure S11. SEM images of microstructures made from 0.5 mM **1** at 80 ºC in various solvents: (a) CH_2Cl_2, (b) ethyl acetate, (c) benzene, (d) toluene, and (e) 1,4-dioxane. The scan bars are 5 μm (a, c-d), and 15 μm (b), respectively.

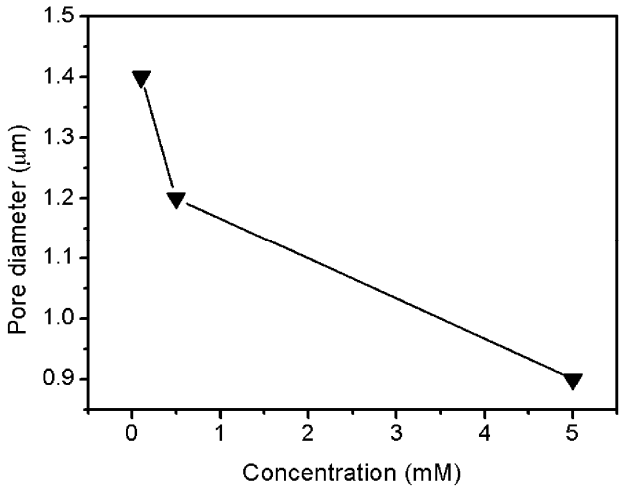


Figure S12. Plot of pore diameter versus concentration of **1** in $CHCl_3$.

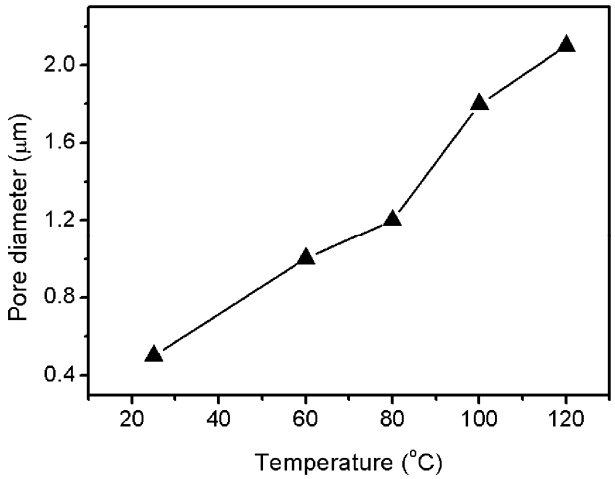


Figure S13. Plot of pore diameter versus temperature.

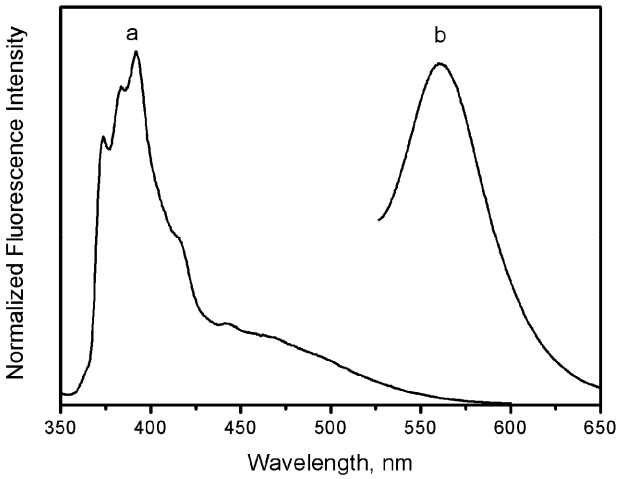


Figure S14. Fluorescence spectra of the honeycomb films made from 0.5 mM **1** at 80 ºC, containing 0.01 equivalents of pyrene (a) and rhodamine 6G (b). Excitation wavelengths were 345 nm (a) and 490 nm (b), respectively.

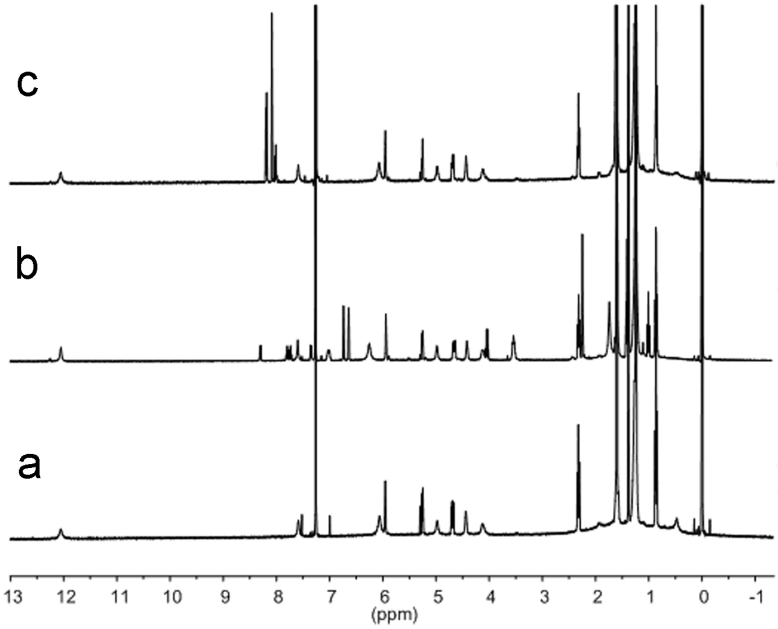
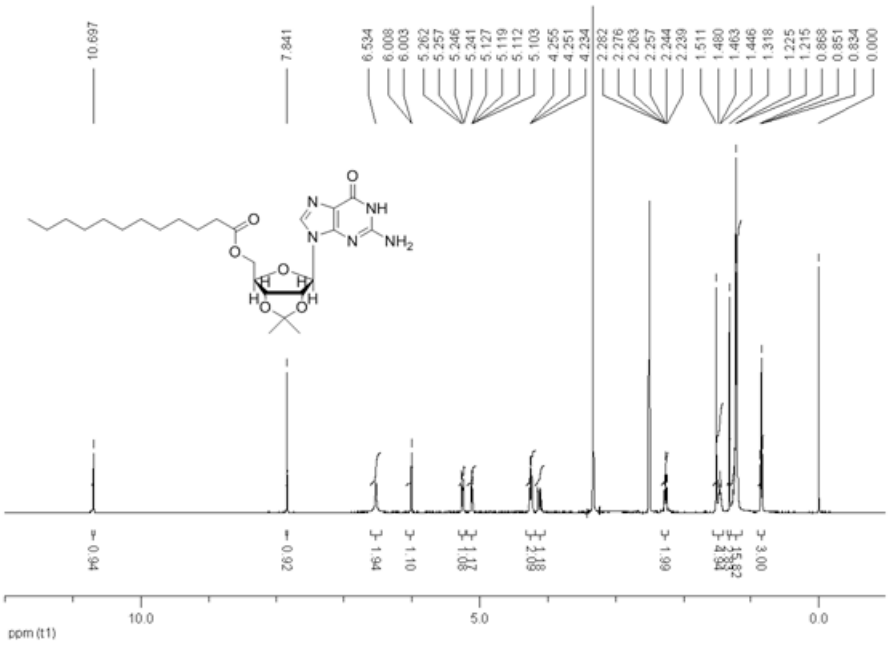
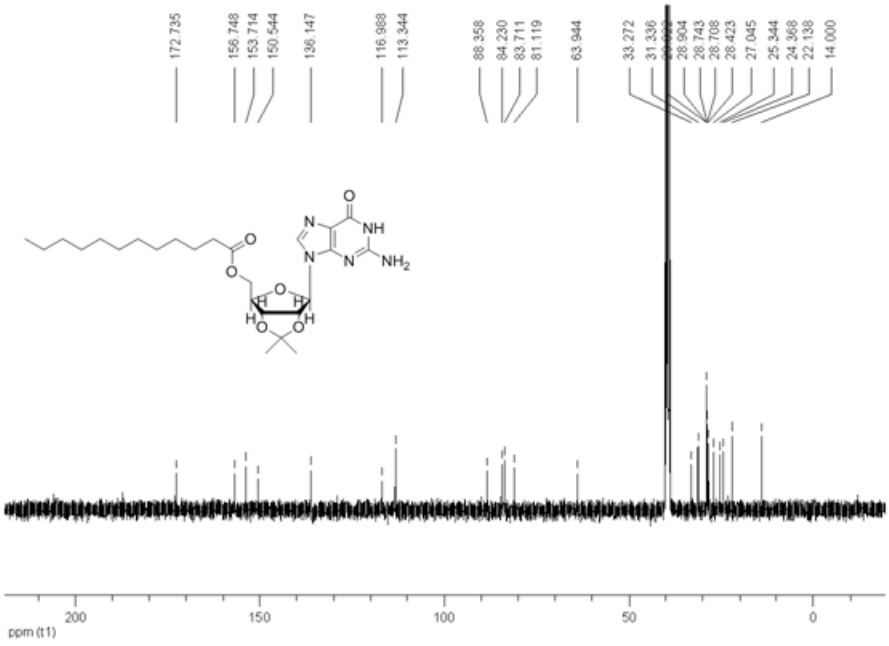
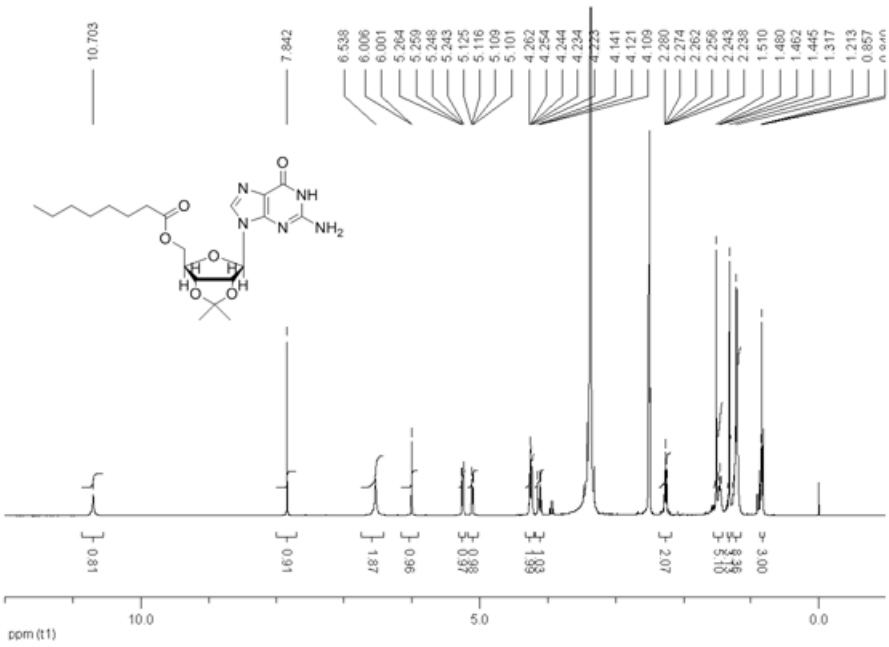


Figure S15. ^{1}H NMR spectra of **1** at 298 K of 10 mM in $CDCl_3$ (a) and in $CDCl_3$ containing 0.2 equivalents of rhodamine 6G (b) or pyrene (c).

^{1}H NMR and ^{13}C NMR spectra of **1**, **2**, **3** and **4**.



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2.256
2.243
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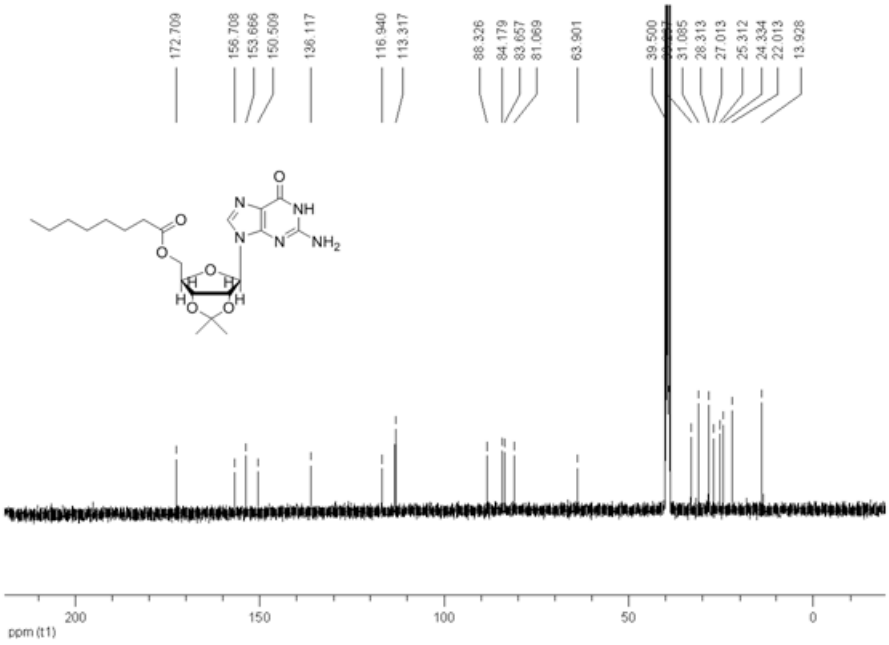
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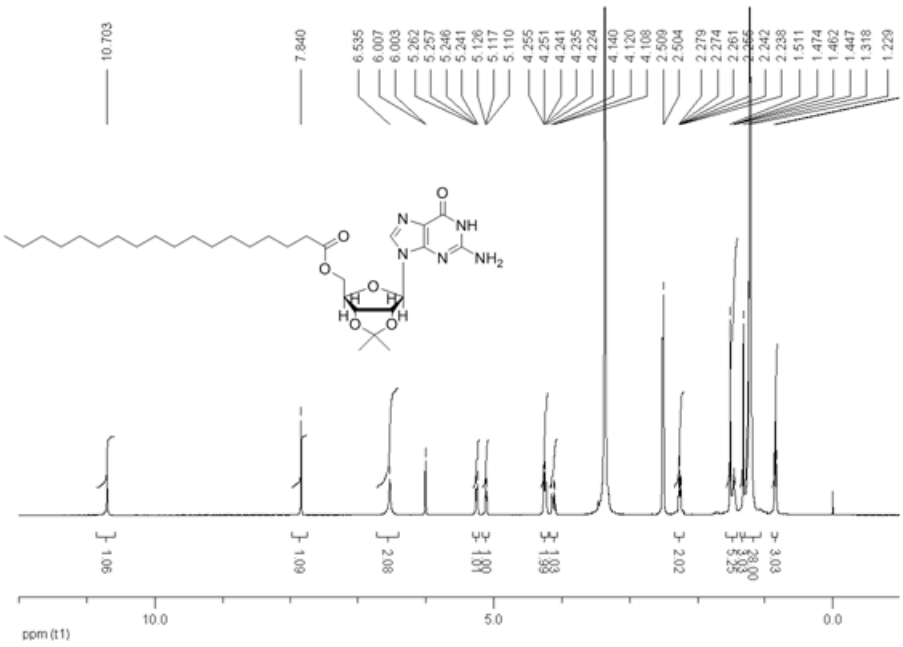
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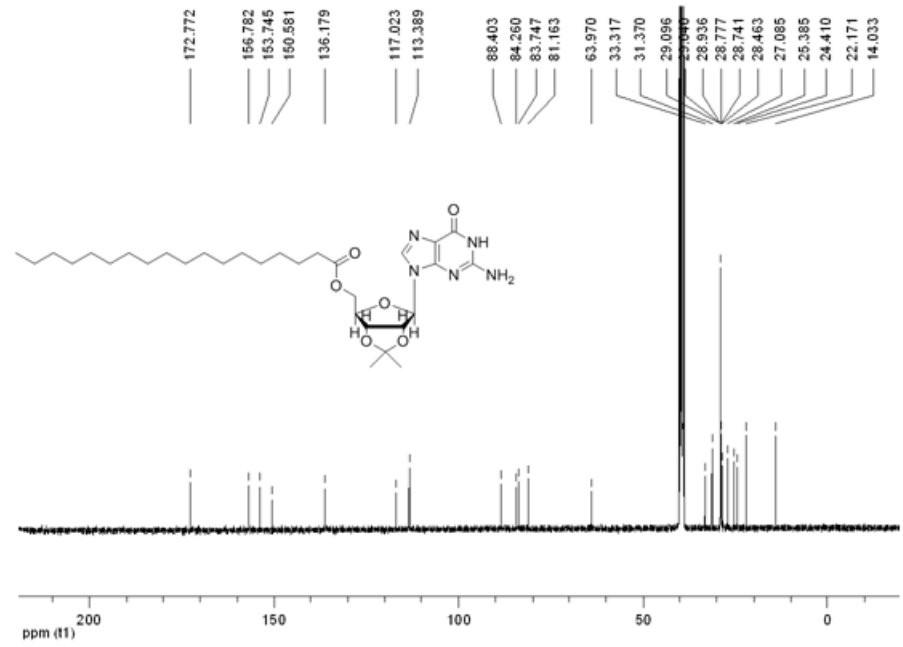
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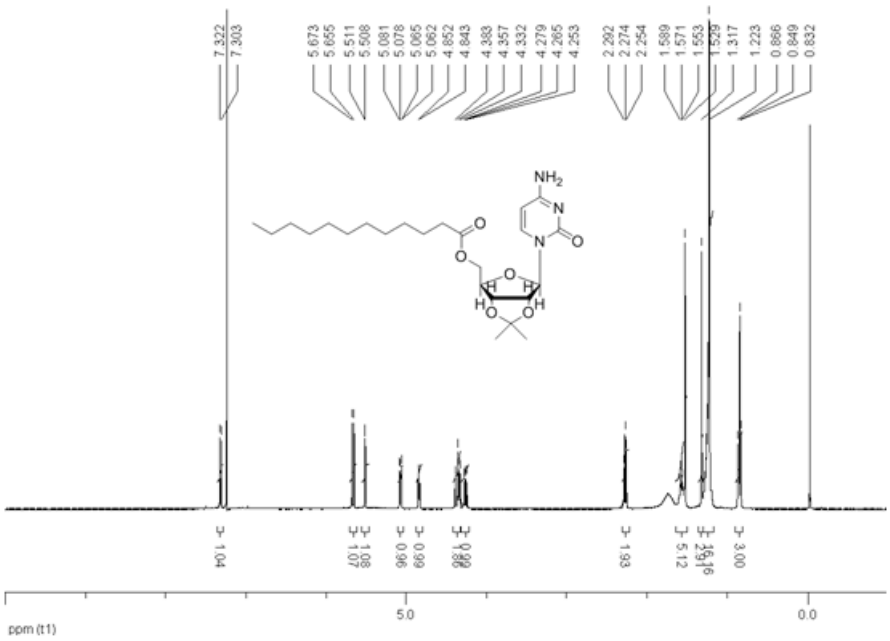
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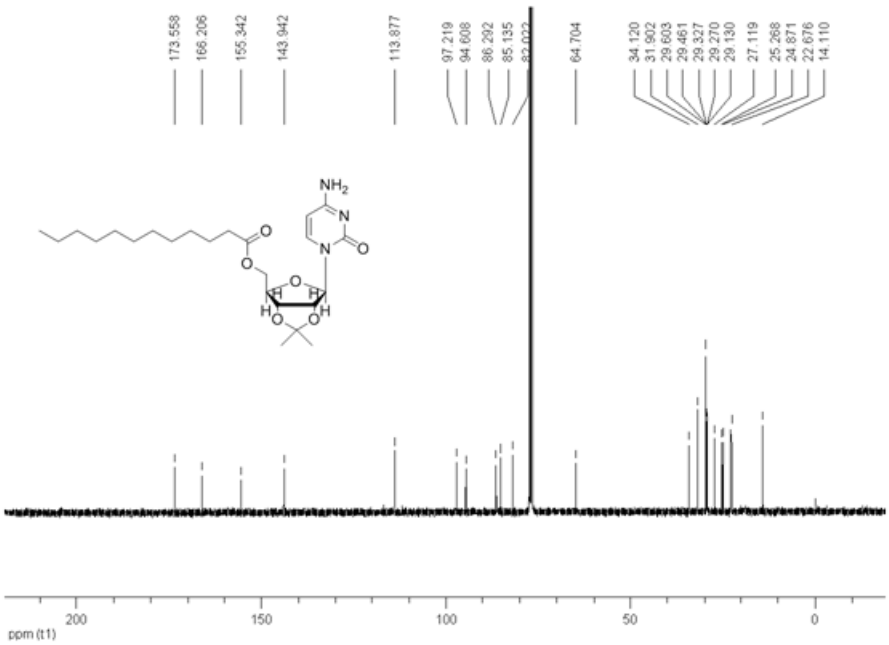
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