

Charge-transfer interaction mediated organogels from 18 β -glycyrrhetic acid appended pyrene

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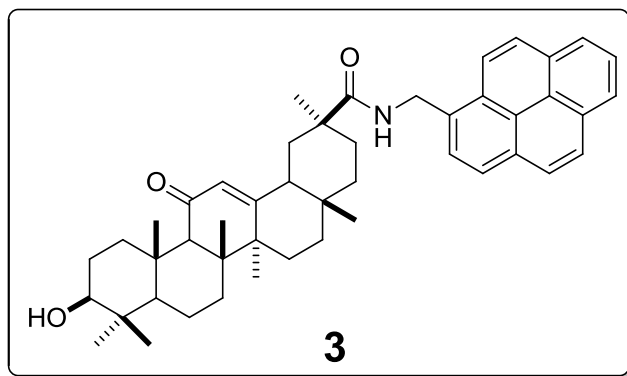
*Corresponding authors

**MS, ¹H NMR and ¹³C NMR spectra of 18 β -glycyrrhetic acid appended
pyrene 3 and 2,4,7-trinitrofluorenone (4); thermodynamic parameters of
CT gel in various solvents**

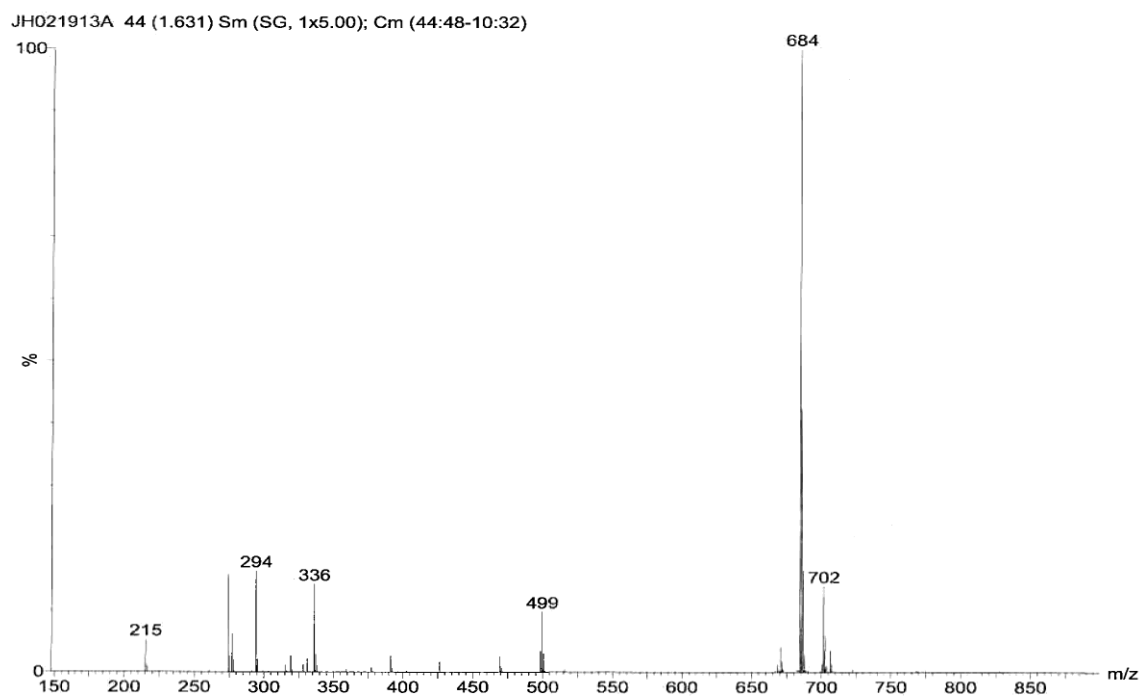
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1. MS, ^1H NMR and ^{13}C NMR spectra of 18 β -glycyrrhetic acid appended pyrene (**3**)



ESI-MS (+) Spectra of 18 β -glycyrrhetic acid appended pyrene **3**



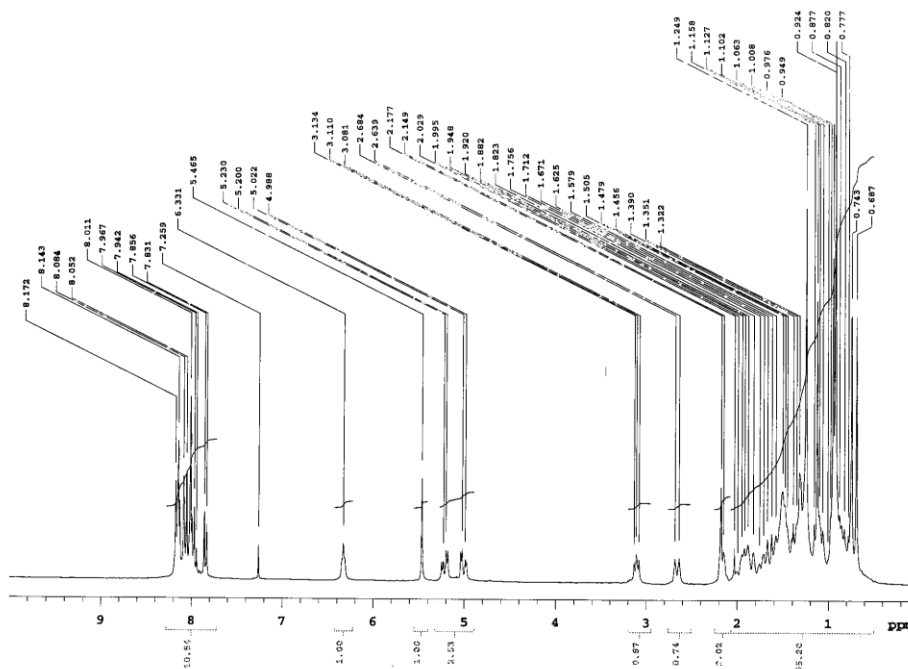
¹H NMR Spectra (CDCl₃, 300 MHz) of 18β-glycyrrhetic acid appended pyrene **3**

YY-65

Sample ID: s_20130225_01
File: 002223.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: nmr
File: 002223
Mercury-300MB "nmr-m300a"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
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16 repetitions
OBSERVE H1, 300.1044985 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 32768
Total time 1 min, 6 sec



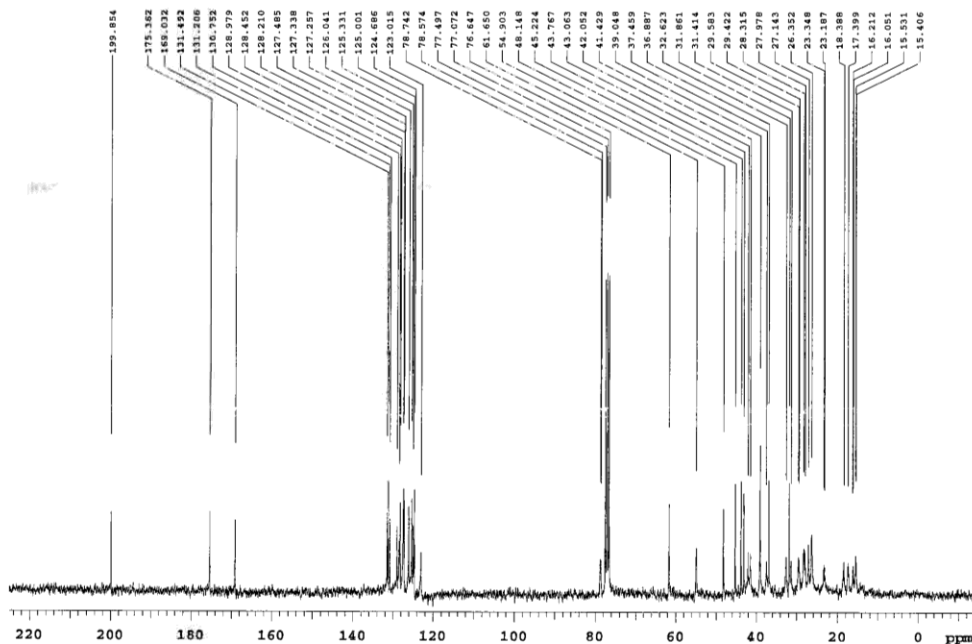
¹³C NMR Spectra (CDCl₃, 75 MHz) of 18β-glycyrrhetic acid appended pyrene **3**

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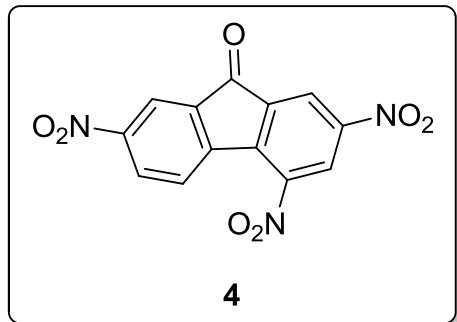
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Solvent: cdcl3
Ambient temperature
Operator: nmr
File: 002223
Mercury-300MB "nmr-m300a"

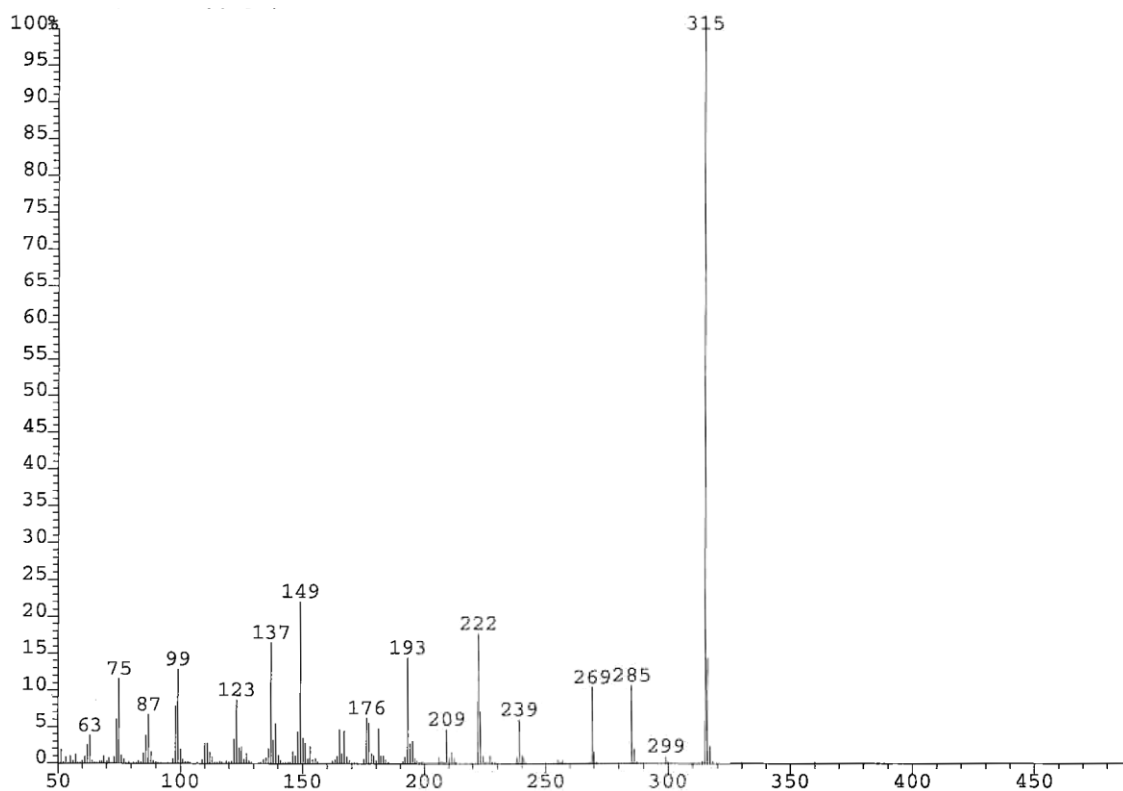
Relax. delay 1.000 sec
Pulse 45.2 degrees
Acq. time 1.301 sec
Width 18119.9 Hz
512 repetitions
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DECOUPLE H1, 300.1060090 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 3.0 Hz
FT size 65536
Total time 21 min, 31 sec



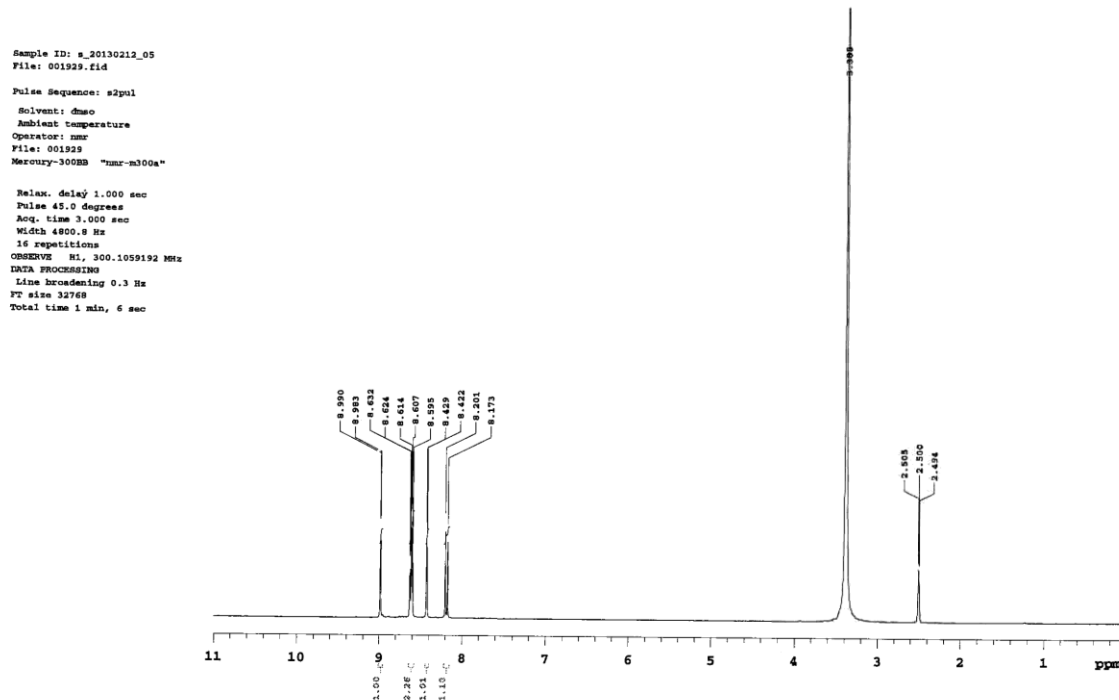
2. MS, ^1H NMR and ^{13}C NMR spectra of 2,4,7- trinitrofluorenone (**4**)



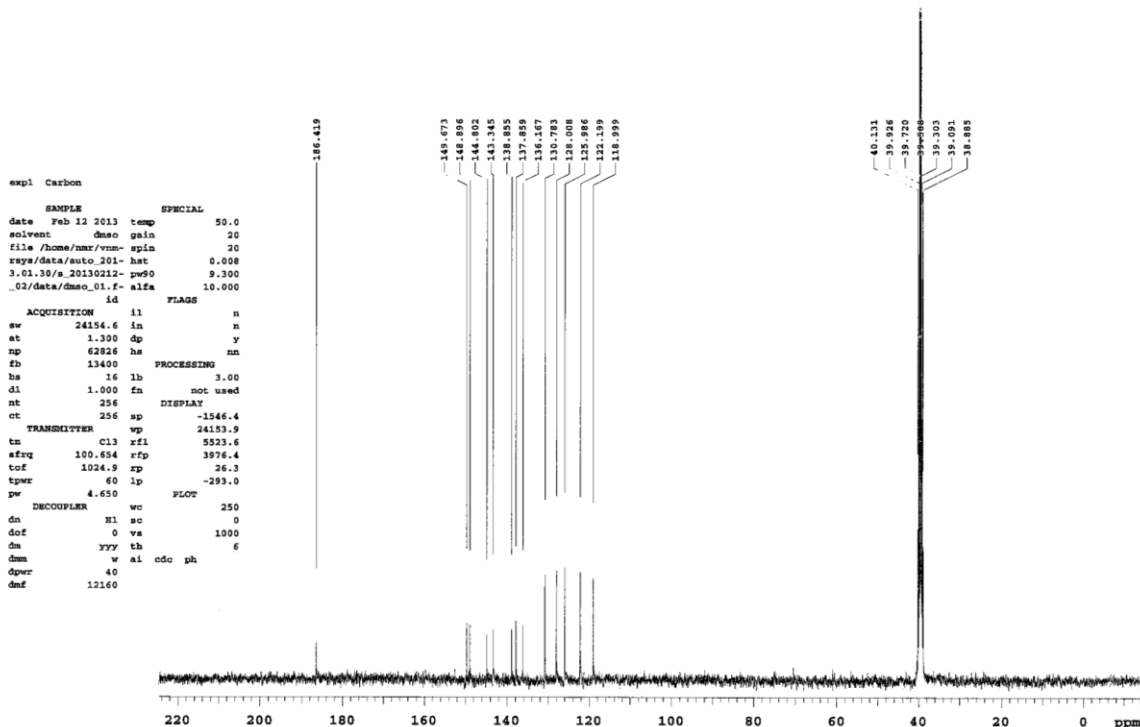
EI-MS (+) Spectra of 2, 4, 7-trinitrofluorenone (**4**)



¹H NMR Spectra (DMSO, 300 MHz) of 2, 4, 7-trinitrofluorenone (**4**)

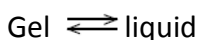


¹³C NMR Spectra (DMSO, 75 MHz) of 2, 4, 7-trinitrofluorenone (**4**)



3. Thermodynamic parameters of CT gel in various solvents [1,2]

The thermoreversible melting of a two component gel can be expressed as:



For one component gel, the equilibrium constant can be expressed as:

$$K = [\text{Gelator}] / [\text{Gel}]$$

Assuming unit activity of the gel and taking the concentration of the solution to be equal to the dissolved concentration of the gelator, the equilibrium constant can be expressed as:

$$K = [\text{Gelator}].$$

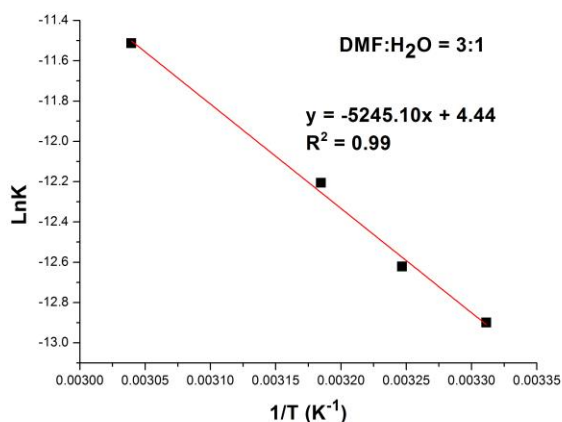
The Gibbs free energy change during gel melting can be expressed as:

$$\Delta G^\circ = -\Delta RT \ln K = \Delta H^\circ - T \Delta S^\circ,$$

$$\text{Hence, } \ln K = -\Delta H^\circ / R (1/T) + T \Delta S^\circ / R$$

The gel melting temperature (T_{gel}) increases with the concentration of the “solutes”. A plot of $\ln K$ vs $1/T$ allowed us to calculate the thermodynamic parameters.

DMF/H₂O (3:1, v/v)



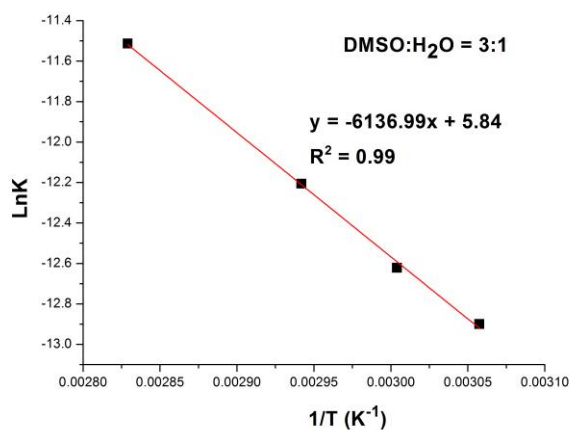
$$\ln K = -5245.10 \times (1/T) + 4.44, R^2 = 0.99$$

$$\Delta H^\circ / R = 5245.10, \Delta H^\circ = 43.1 \text{ kJ/mol};$$

$$\Delta S^\circ / R = 4.44, \Delta S^\circ = 36.9 \text{ J/mol/K}$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 43.1 - 298 \times 0.0369 = 32.1 \text{ kJ/mol}$$

DMSO/H₂O (3:1, v/v)



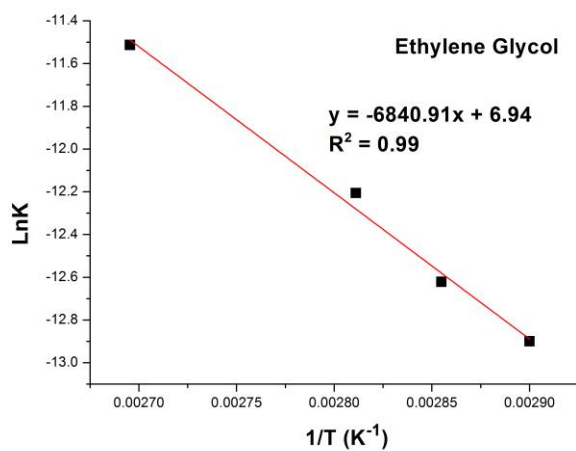
$$\text{Ln}K = -6136.99 \times (1/T) + 5.84, R^2 = 0.99$$

$$\Delta H^0/R = 6136.99, \Delta H^0 = 51.0 \text{ kJ/mol};$$

$$\Delta S^0/R = 5.84, \Delta S^0 = 48.5 \text{ J/mol/K}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 51.0 - 298 \times 0.0485 = 36.5 \text{ kJ/mol}$$

Ethylene Glycol



$$\text{Ln}K = -6840.91 \times (1/T) + 6.94, R^2 = 0.99$$

$$\Delta H^0/R = 6840.91, \Delta H^0 = 56.8 \text{ kJ/mol};$$

$$\Delta S^0/R = 6.94, \Delta S^0 = 57.6 \text{ J/mol/K}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 56.8 - 298 \times 0.0576 = 39.6 \text{ kJ/mol}$$

References

- 1 D. Rizkov, J. Gun, O. Lev, R. Sicsic and A. Melman, *Langmuir*, **2005**, 21, 12130.
- 2 J. Hu, M. Zhang and Y. Ju, *Soft Matter*, **2009**, 5, 4971.