Electronic Supplementary Information

Self-assembly of a renewable nano-sized triterpenoid 18β-glycyrrhetinic acid

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Additional Analytical Data for 18β-glycyrrhetinic acid 1: R_f = 0.3 (20% ethyl acetae-dichloromethane), Mp = 284 °C. FTIR(KBr, cm^{-1}): 3483, 3466, 3427, 3300 – 3600 (br.) 2970 (m), 2928 (m), 2868 (w), 1705 (s), 1666 (s), 1620 (w), 1541 (w), 1456 (m), 1386 (m), 1326 (m). $[\alpha]_D^{298}$ = + 82.7 (methanol, 0.222 g/100 mL) Reversed-phase HPLC analysis (conditions: C_{18}-column, 250 mm x 4.6 mm, mobile phase: methanol (flow rate 0.4 mL/minute, UV-Vis detection at 206 nm.) t_R = 8.83 min.

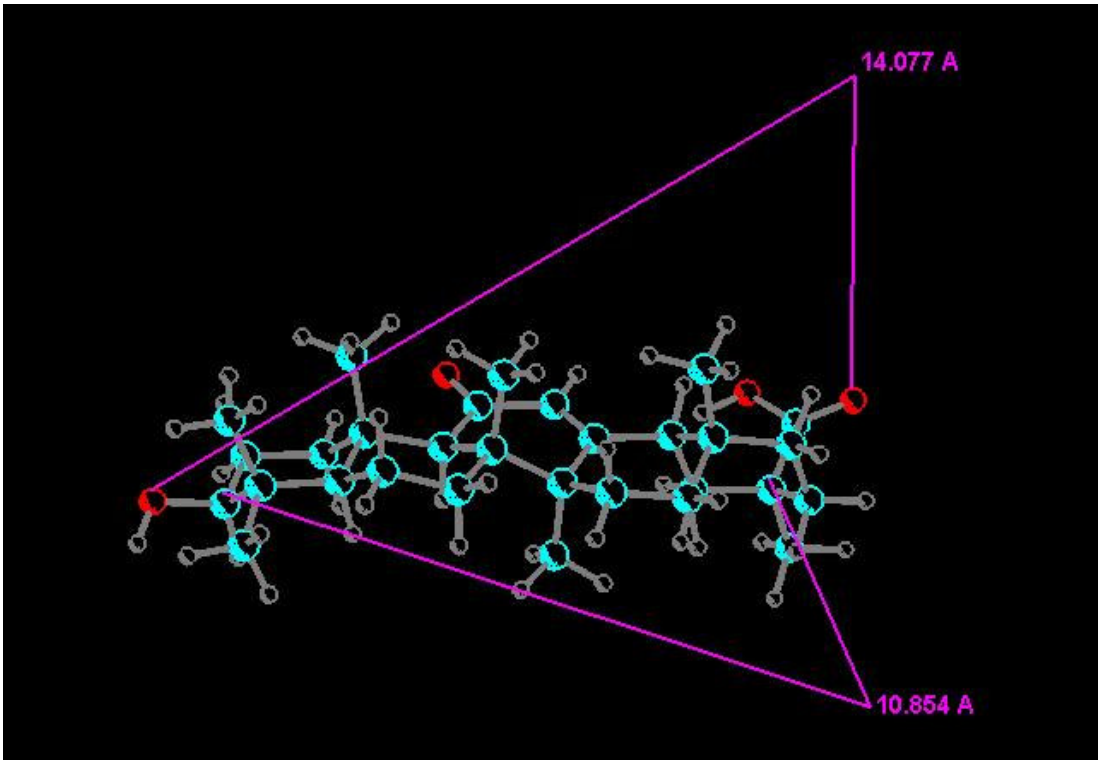

Fig S1: Energy minized structure of 18β-glycyrrhetinic acid 1 using MMX force field as implemented in PCMODEL version 9.2 (serena software)®

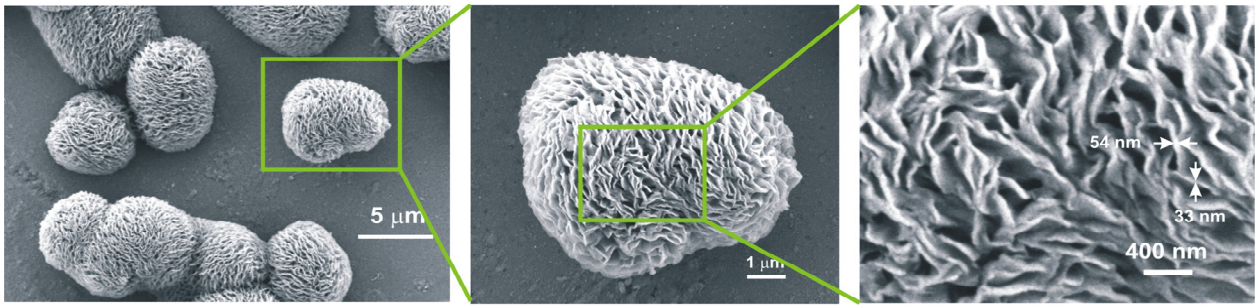

Figure S2: FESEM Image of the xerogel of **1** from o-dichlorobenzene gel (0.25% w/v).These images are recorded in Zeiss FESEM.

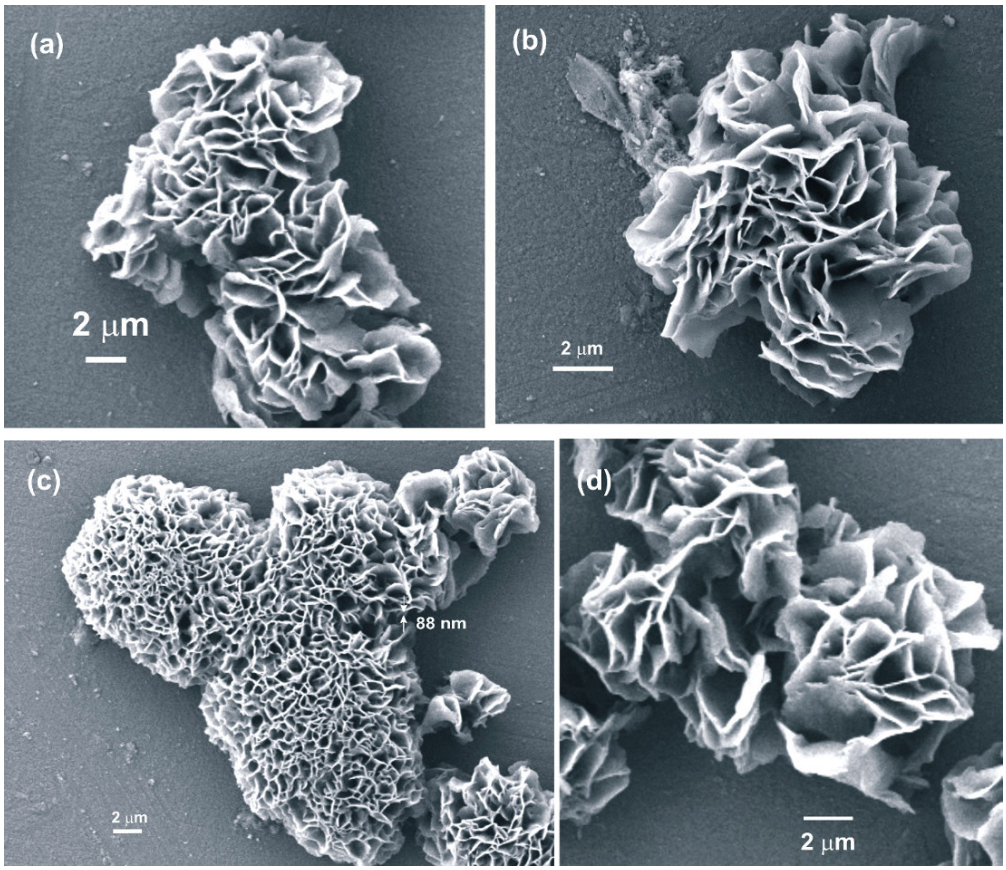

Figure S3: FESEM of the xerogels of **1** from nitrobenzene gel (0.25% w/v). These images are recorded in Zeiss FESEM.

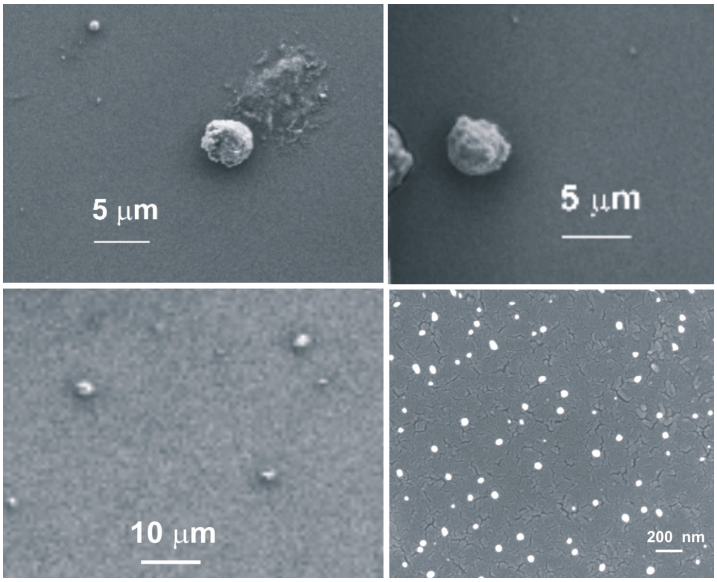

Figure S4: FESEM of the xerogels of **1** from 5:2 DMSO-water gel (0.045% w/v). These images are recorded in Zeiss FESEM.

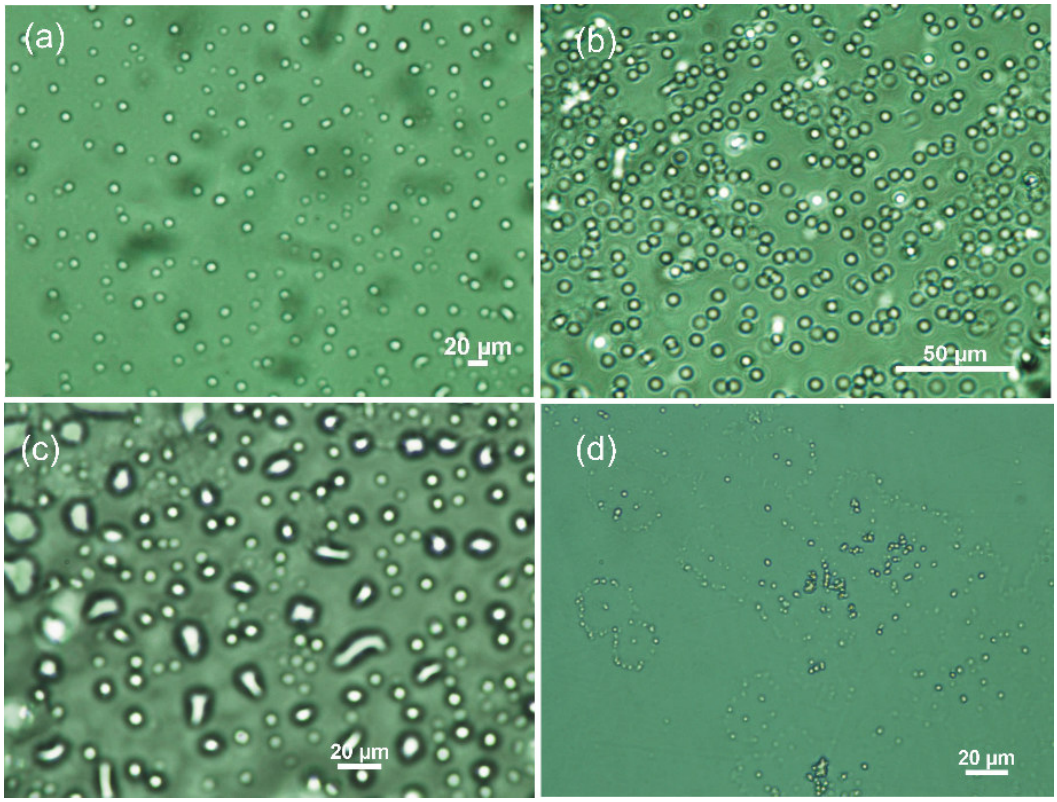

Figure S5. Polarizing Optical microscopic images of 18β-glycyrrhetinic acid **1** gel (recorded in NIKON ECLIPSE LV100POL instrument.): (a) OPM images of ethylene glycol partial gel of **1** (0.91 % w/v) (b) OPM image of p-methoxy benzaldehyde partial gel of **1** (1.25 % w/v) (c) OPM image of the o-dichloro benzene partial gel of **1** (3.33% w/v), (d) OPM image of a nitrobenzene partial gel of **1** (2.5% w/v). The aliquot of sample taken on a cover slip was covered with another cover slip and placed under the microscope.

AFM IMAGES

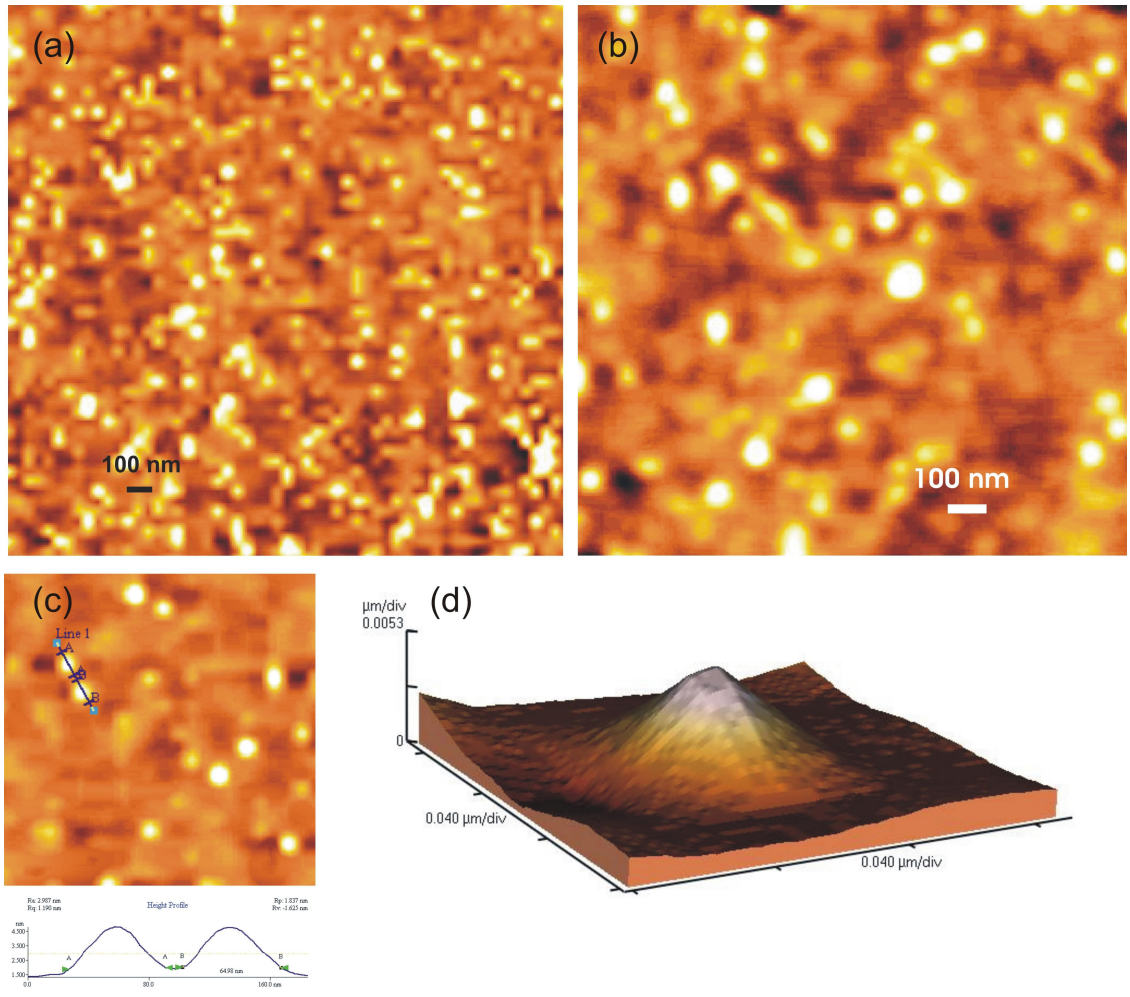

Figure S6: AFM images of 18β-glycyrrhetinic acid in p-methoxybenzaldehyde (1.25% w/v). In image (c) the diameters of the left and right spherical objects are 63.54 and 64.98 nm respectively. Images were captured in atomic force microscopy VEECO, dicp-II, Model no. AP0100. A solution of the sample (1.25% w/v) was coated on a glass plate and allowed to dry in air for over night and then under reduced pressure.

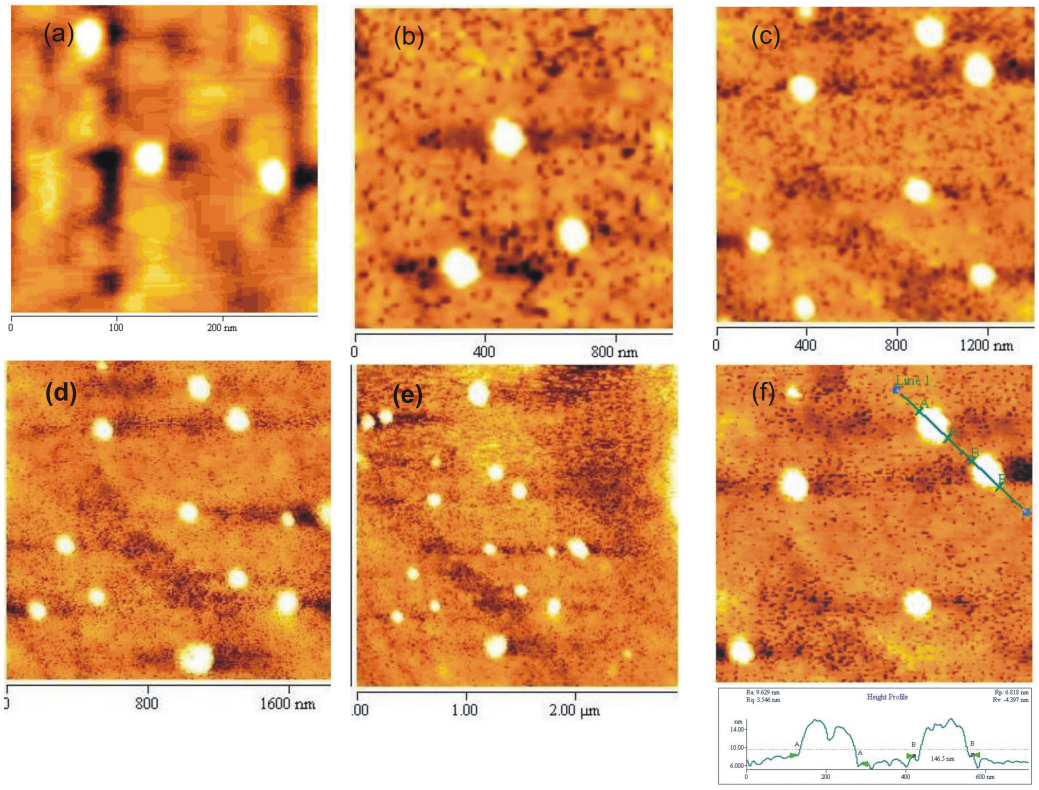

Fig S7: AFM Images of 1in DMSO-water

Images were captured in atomic force microscopy VEECO, dicp-II, Model no. AP0100. A hot solution of sample in DMSO - water (0.045% w/v, ratio 5:2) was allowed to cool at room temperature and then coated on a glass plate and allowed to dry in air for over night and then under reduced pressure.

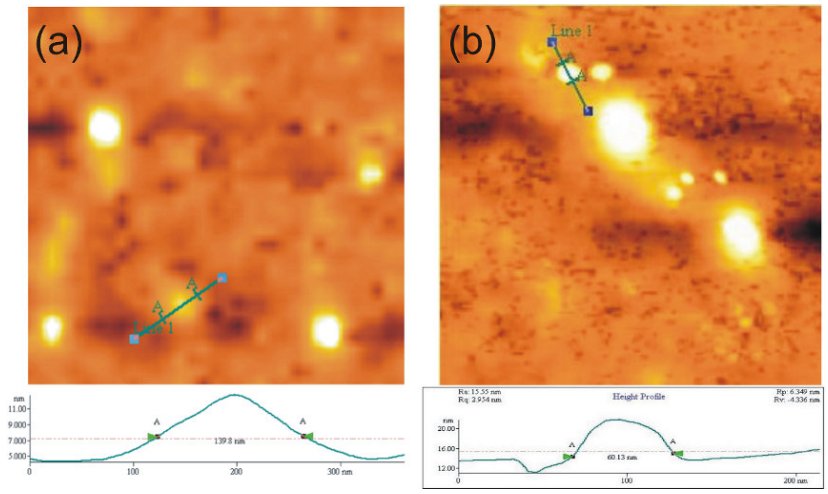

Fig S8: AFM images of 1 in nitrobenzene: Images were captured in atomic force microscopy VEECO, dicp-II, Model no. AP0100. A solution of the sample in nitrobenzene (0.25 %w/v) was coated on a glass plate and allowed to dry in air for over night and then under reduced pressure. Spherical shape objects of nano-meter –micrometer ranges were obtained.

Thermodynamic parameters[1]

Calculation:

The thermoreversible melting of a gel can be expressed as :

$$\text{Gel} \rightleftharpoons \text{liquid}$$

The equilibrium constant can be expressed as :

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

Assuming unit activity of the gel, the equilibrium constant can be expressed as :

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

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

$\Delta G^0 = -RT\ln K = \Delta H^0 - T\Delta S^0$, Hence, $\ln K = -\Delta H^0/R.\ (1/T) + \Delta S^0/R$

The gel melting temperature (T_{gel}) increases with increasing concentration of the "solutes". A plot of lnK vs 1/T allowed us to calculate the thermodynamic parameters . A representative plot for a gel in chlorobenzene is given in the figure below:

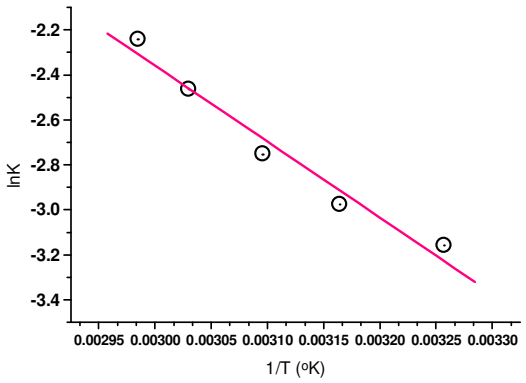

Figure S9

From the slope we obtain $-\Delta H^0/R = -3379.00237$ and from the intercept we obtain $\Delta S^0/R = 7.7784$

The thermodynamic parameters are : $\Delta S^0 = 64.67$ J/mol/°K, $\Delta H^0 = 28.09$ kJ/mol and $\Delta G^0 = 8.82$ kJ/mol

[1] Rizkov, D.; Gun, J.; Lev, O.; Sicsic, R.; Melman, A. *Langmuir* 2005, **21**, 12130.

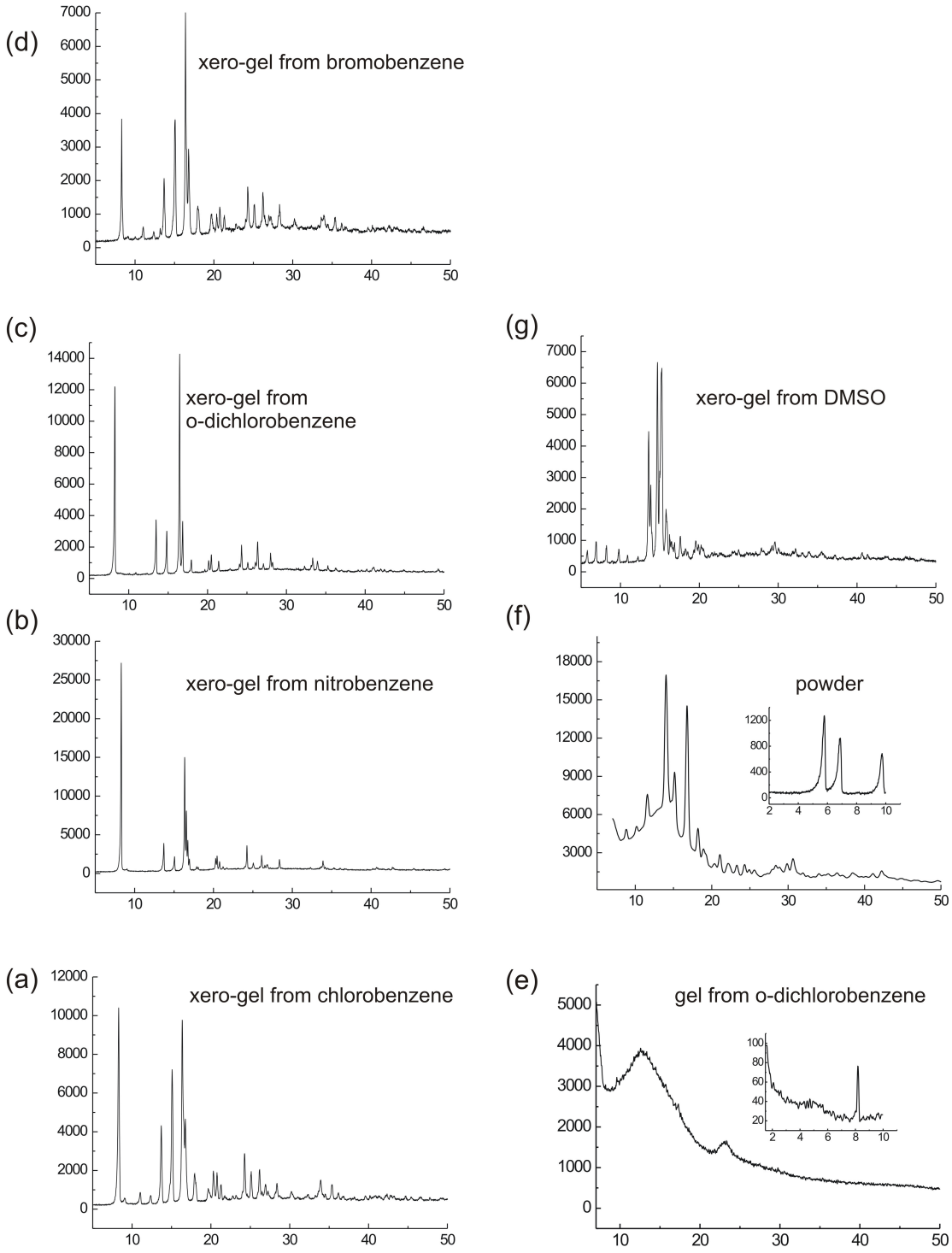

Fig. S 10: X-RAY diffractograms have been recorded in a **Bruker** X-ray diffractometer at room temperature (25 °C) using Cu-Kα filament (λ = 1.54 Å) .

Table S1: Wide angle X-ray diffraction data of 18β-glycyrrhetinic acid under different conditions

Sample	d (Å)
Xerogel from $PhNO_2$	10.6, 6.5, 5.9, 5.4, 5.3, 4.9, 4.4, 4.3, 3.7, 3.6, 3.4, 3.3, 3.2, 2.7, 2.5
Xerogel from PhCl	10.7, 6.5, 5.9, 5.4, 5.3, 4.9, 4.5, 4.3, 4.2, 3.7, 3.6, 3.4, 3.3, 2.5
Xerogel from PhBr	10.7, 6.5, 5.9, 5.4, 5.3, 4.9, 4.5, 4.4, 4.3, 4.2, 3.7, 3.5, 3.4, 3.3, 3.2, 2.5
Xerogel from o-$PhCl_2$	10.7, 6.6, 5.9, 5.4, 5.3, 4.9, 4.4, 4.3, 4.2, 3.7, 3.6, 3.4, 3.3, 3.2, 2.8, 2.5
Xerogel from DMSO	15.3, 12.7, 10.8, 9.0, 6.5, 6.4, 6.0, 5.8, 5.6, 4.9, 4.5, 4.4, 4.3, 3.6, 3.2, 2.7, 2.5
Powder	15.2, 12.9, 9.1, 8.7, 7.6, 6.3, 5.9, 5.3, 4.9, 4.7, 4.4, 4.2, 4.0, 3.8, 3.7, 3.6, 3.5, 3.2, 3.0, 2.9, 2.8, 2.6
Gel in o-dichlorobenzene	10.8, 6.5, 5.5, 5.2, 5.1, 3.8, 3.7

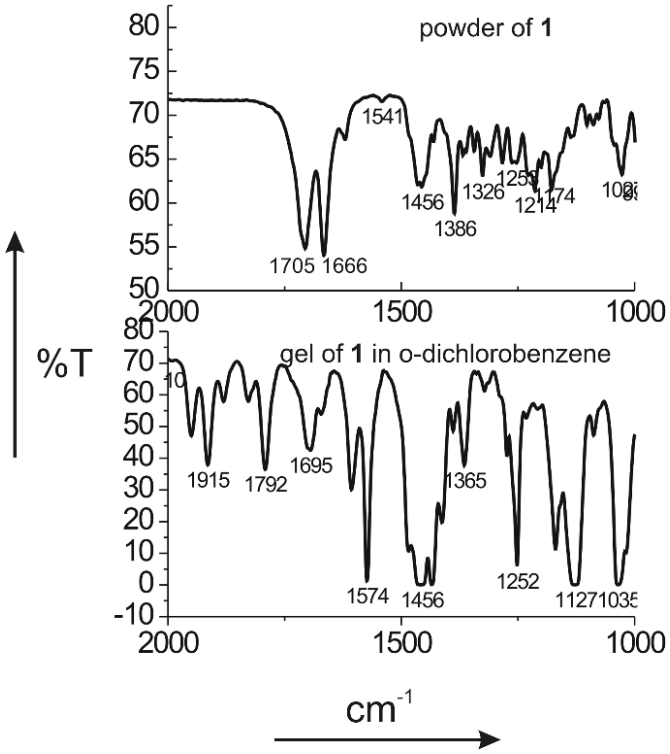

Figure S11a: Overlay of FTIR spectra showing the shift of 'C=O' stretching frequency of the carboxyl group of glycyrrhetinic acid from 1705 cm^{-1} in a powder sample to 1695 cm^{-1} in a gel sample in o-dichlorobenzene (4% w/v).

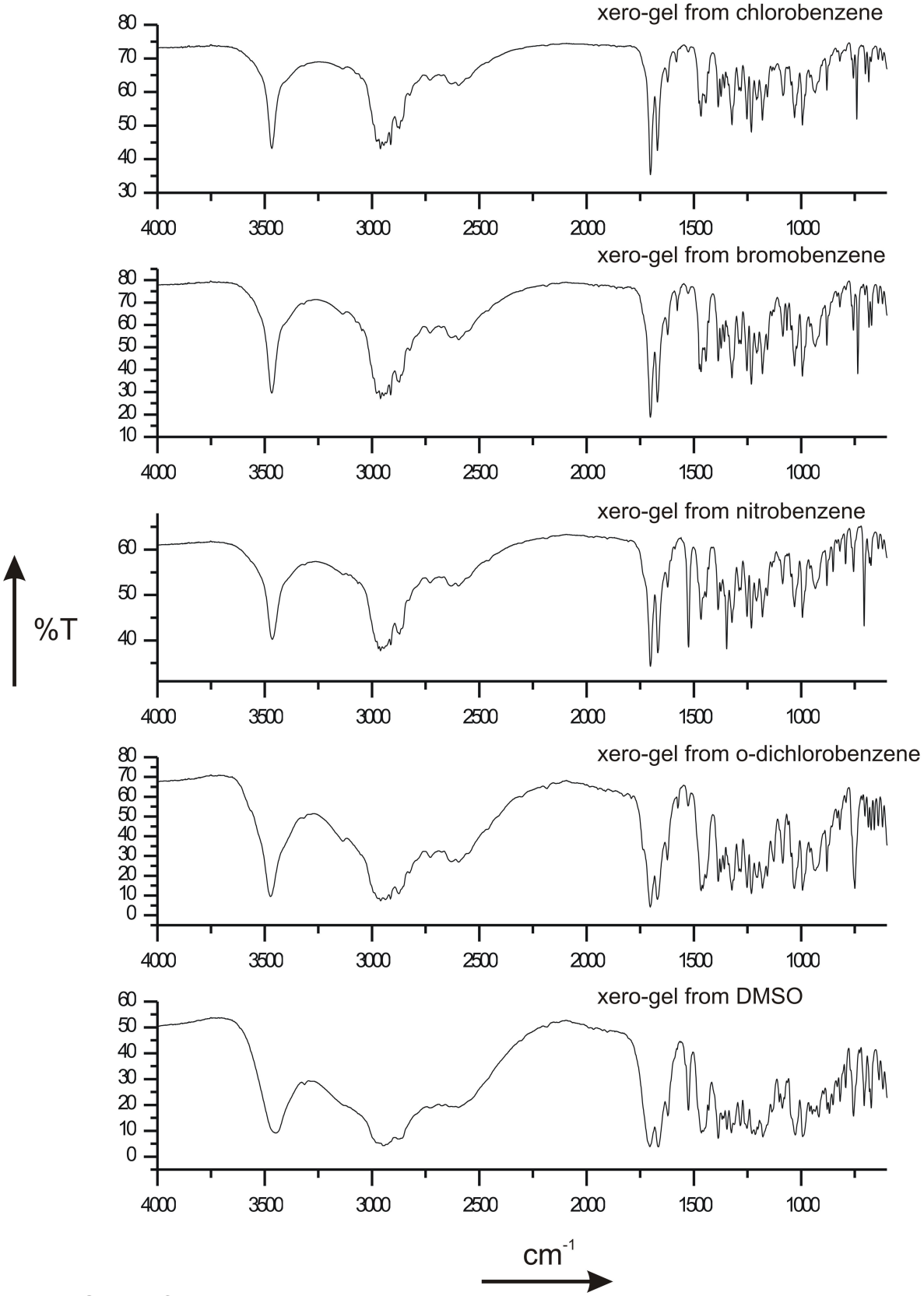

Figure S 11b: Overlay of FTIR spectra (KBr) of the xerogels obtained from different solvents

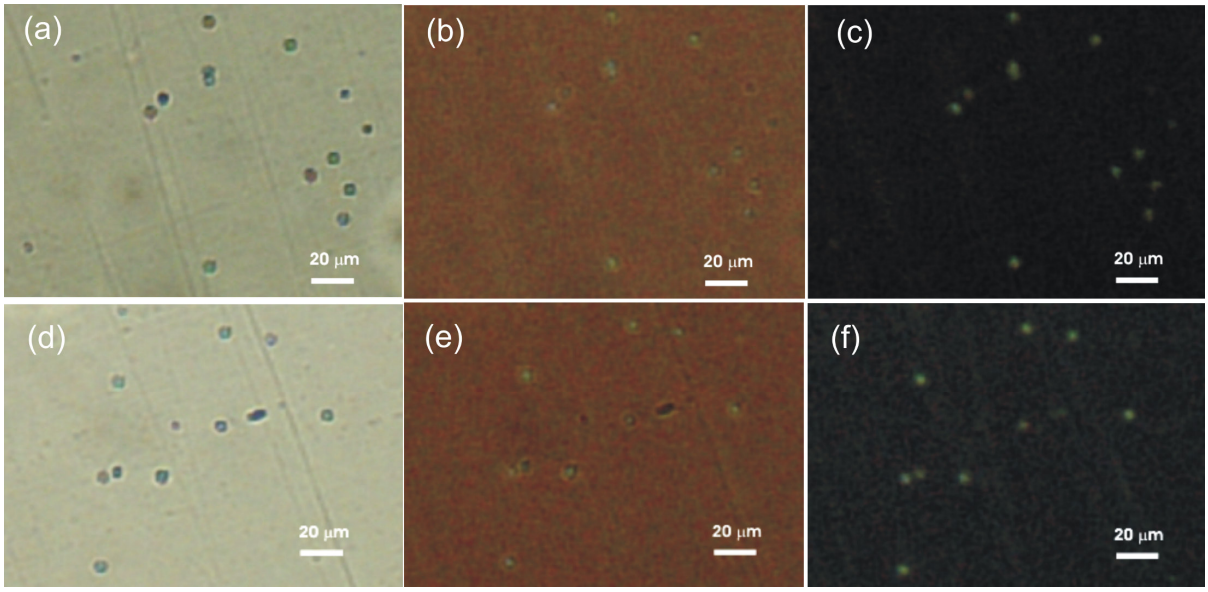

Figure S12. (a-f) Epifluorescent microscopy images of a partial gel of 18β-glycyrrhetinic acid in ethylene glycol (1% w/v) containing CdS nano particle: (a,d) bright field images, (b,e) overlay images, (c,f) fluorescent images.

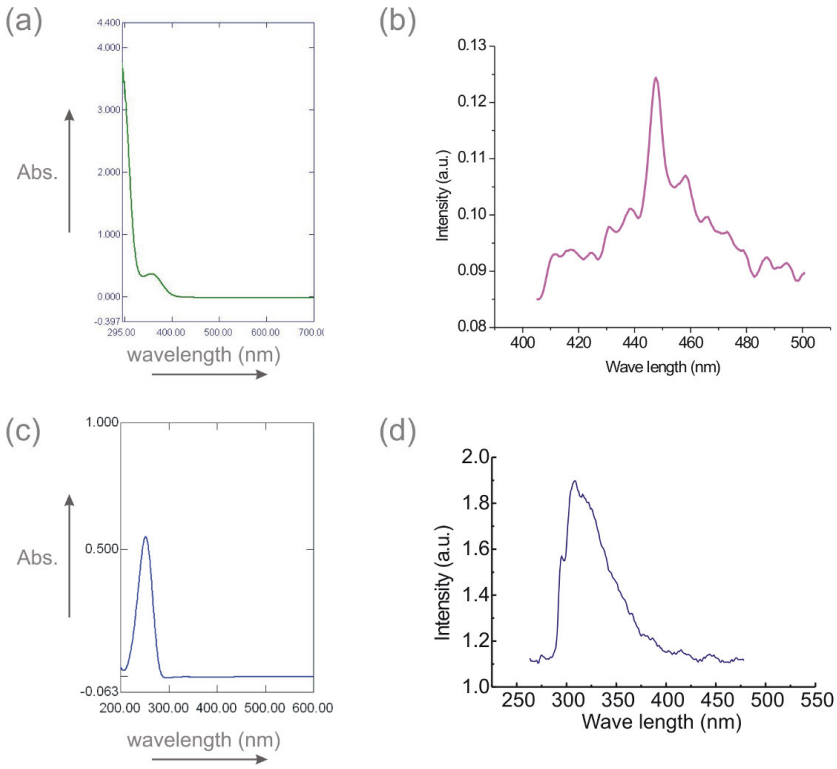

Figure S13: (a) UV-Vis spectrum of templated CdS nanoparticle on self-assembled 18β-glycyrrhetinic acid (0.1% w/v) in ethylene glycol, (b) fluorescence emission spectrum upon excitation at 395 nm, (c) UV-Vis spectrum of 18β-glycyrrhetinic acid (0.21 mM) in ethylene glycol; (d) fluorescence emission spectrum of 18β-glycyrrhetinic acid upon excitation at 252 nm.

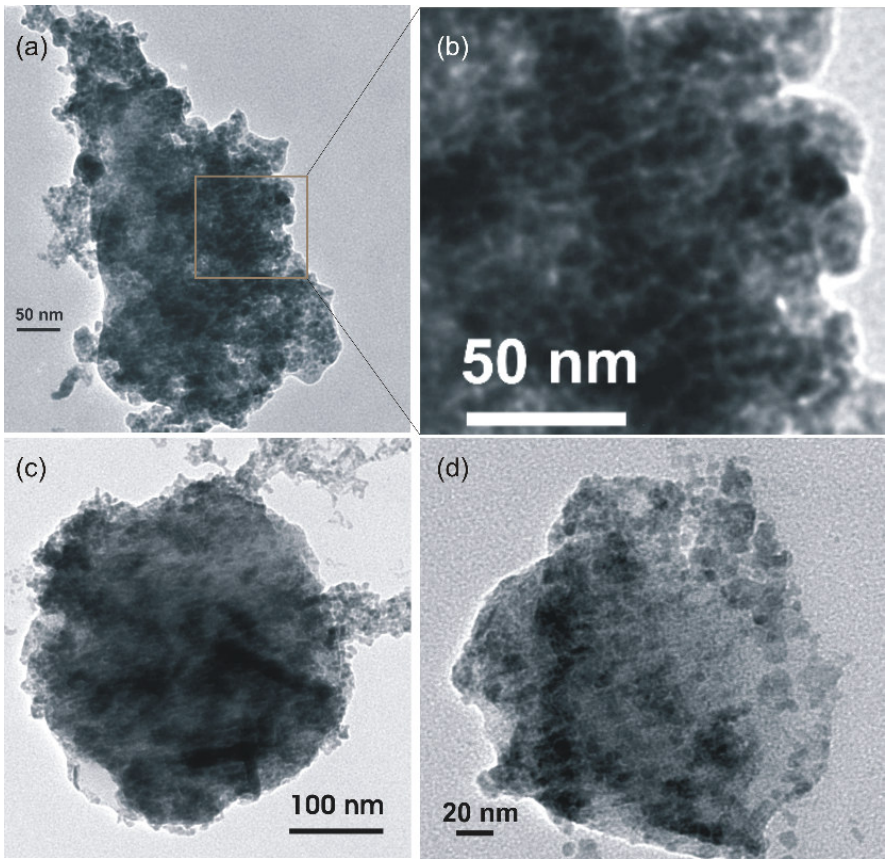

Figure S14: Transmission electron microscopy images of CdS nanoparticles deposited on the self-assemblies of 18β-glycyrrhetinic acid (1% w/v).

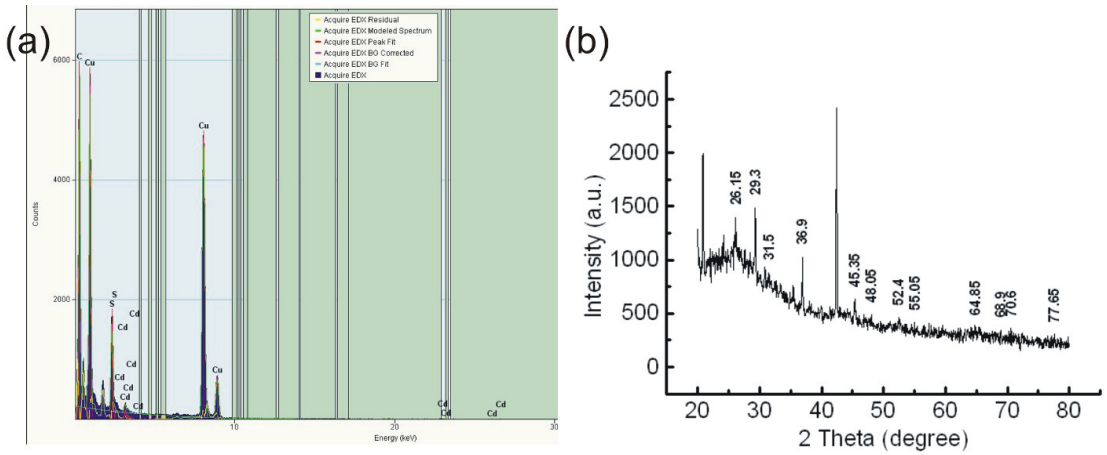

Figure S15: (a) Energy dispersive X-ray spectrum of templated CdS nanoparticles embedded on the self-assemblies of 18β-glycyrrhetinic acid (1% w/v) in ethylene glycol; (b) X-ray diffractogram of CdS nanoparticles (ref. JCPDS 030-65-2887 for cubic CdS and JCPDS File No. 2-549 for hexagonal CdS) embedded on 18β-glycyrrnetinic acid self-assemblies.