

Supplementary Material (ESI) for RSC Advances

Organogels of triterpenoid–tripeptide conjugates: encapsulation of dye molecules and basicity increase associated with aggregation

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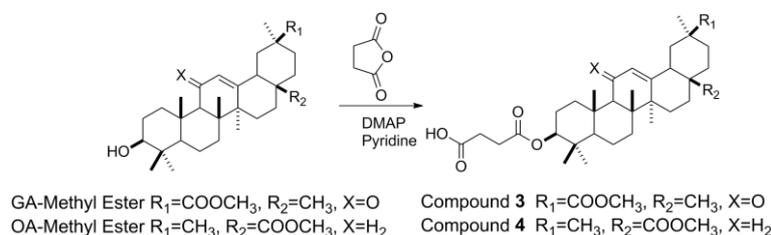
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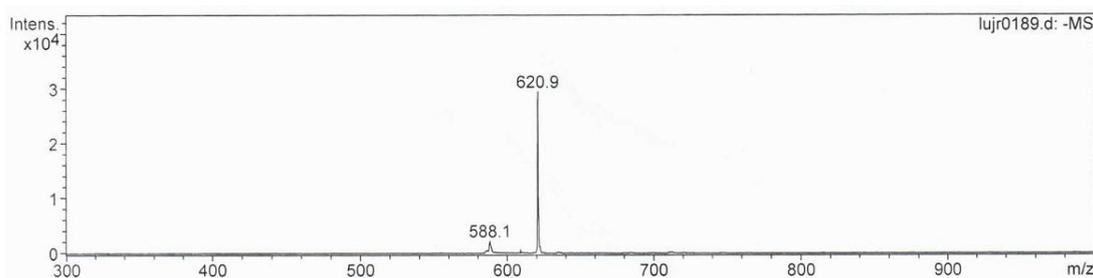
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1. Synthesis of compound **3** and **4**

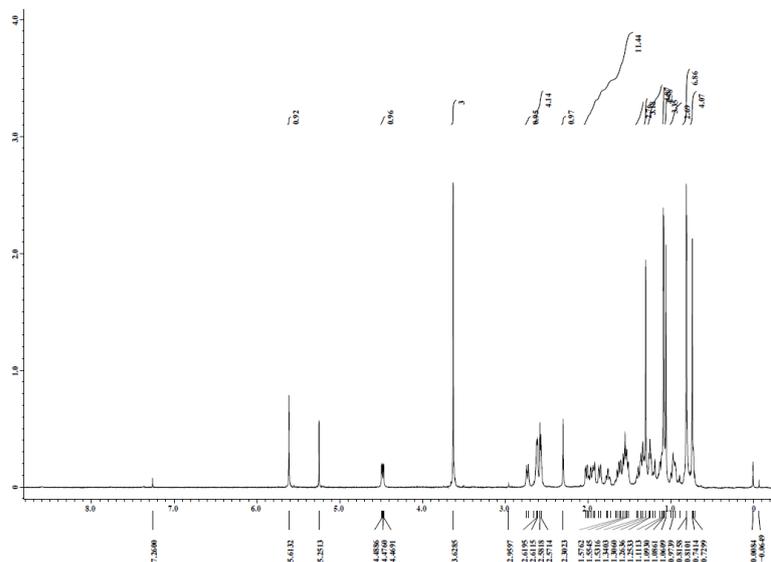


To the solution of 490 mg (4.9mmol) of succinic anhydride and DMAP (6 mg) in 20 ml of pyridine, 500 mg (1.03mmol) of GA-Methyl ester was added. The reaction mixture was stirred at 80°C for 17 h. The reaction mixture was cooled to room temperature, poured into 50 ml of water. The mixture was then extracted with dichloromethane and organic phase was separated and washed with water (30 ml) and brine (30 ml), dried by MgSO_4 and evaporated. The solid was purified by silica gel column chromatography (CH_2Cl_2 : CH_3OH = 40:1) afforded **3** as a yellow solid (280 mg, 47%). ESI-MS m/z : 620.9 $[\text{M}+\text{Cl}]^-$, ^1H NMR (300MHz, CDCl_3): 5.61(s, 12-H, 1H), 4.48(dxd, 3-H, 1H, $J_1=4.8$ Hz, $J_2=12.0$ Hz), 3.63(s, -COOCH₃, 3H), 0.73, 0.80, 0.81, 1.05, 1.08, 1.08, 1.30 (7xs, 7x3Hx2, 23, 24, 25, 26, 27, 28, 29-CH₃). ^{13}C NMR (75 MHz, CDCl_3): 200.31(11-CO), 177.76(-COOH), 177.04(30-COOme), 171.94(3-COO-), 169.63(13-C), 128.42(12-C).

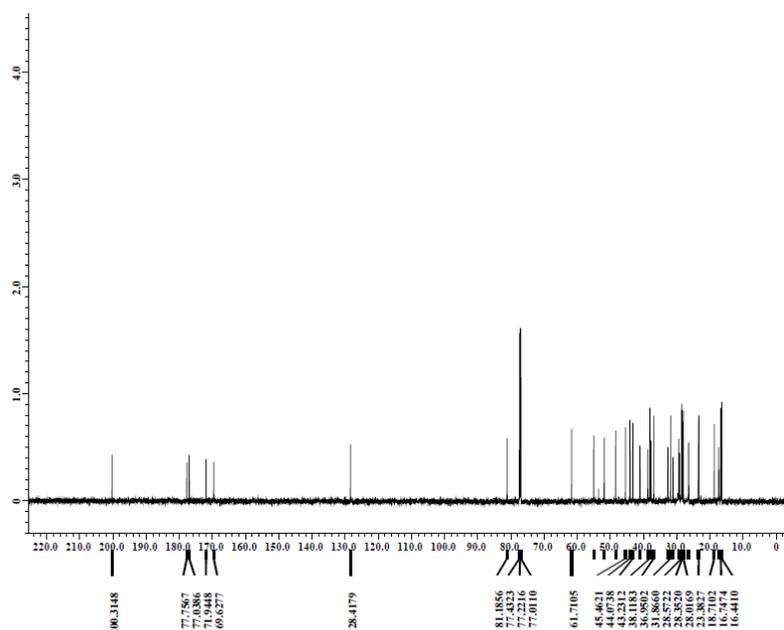
1)ESI-MS (-) Spectra of compound **3**



2) ^1H NMR Spectra of compound **3** (CDCl_3 , 300MHz)

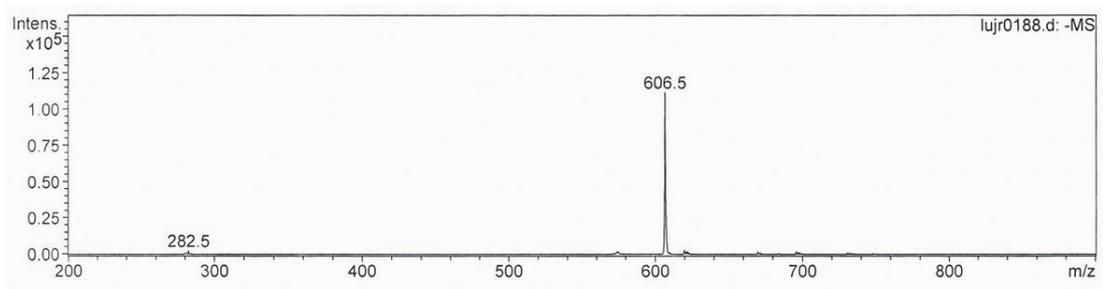


3) ^{13}C NMR Spectra of compound **3** (CDCl_3 , 75MHz)

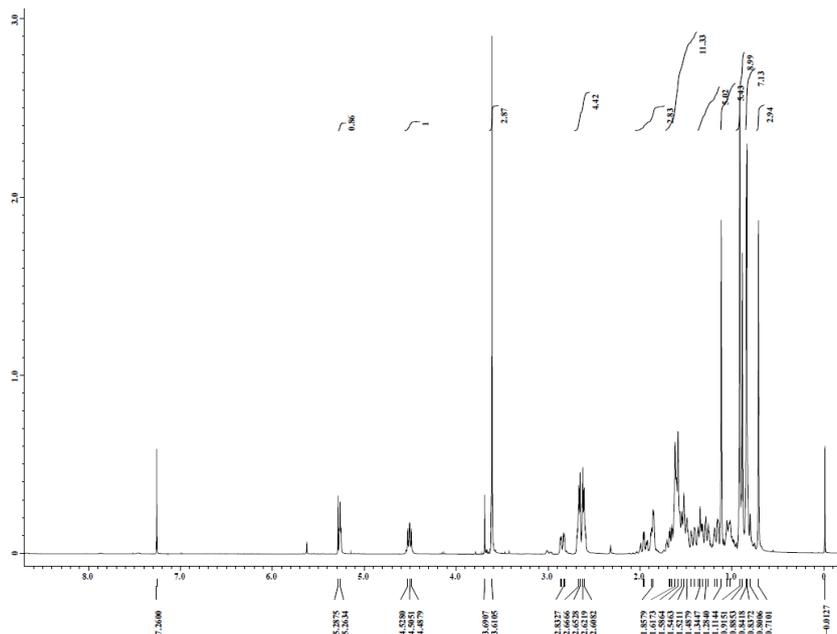


The compound **4** was synthesized by using the same procedure as that described for **3**. ESI-MS m/z : 606.5 $[\text{M}+\text{Cl}]^-$, ^1H NMR (400MHz, CDCl_3): 5.26(t, 12-H, 1H), 4.50(t, 3-H, 1H), 3.61(s, $-\text{COOCH}_3$, 3H), 1.11, 0.92, 0.92, 0.89, 0.84, 0.83, 0.71(7 \times s, 7 \times 3H \times 2, 23, 24, 25, 26, 27, 28, 30- CH_3). ^{13}C NMR (100 MHz, CDCl_3): 178.28($-\text{COOH}$), 177.94(30- COOMe), 171.77(3- $\text{COO}-$), 143.74(13-C), 122.22(12-C), 81.48, 55.27, 51.48, 47.49, 46.68, 45.80, 41.59, 41.25, 39.24, 38.03, 37.68, 36.87, 33.80, 33.05, 32.54, 32.32, 30.63, 29.29, 29.02, 27.92, 27.63, 25.85, 23.58, 23.38, 23.02, 18.16, 16.77, 16.64, 15.29

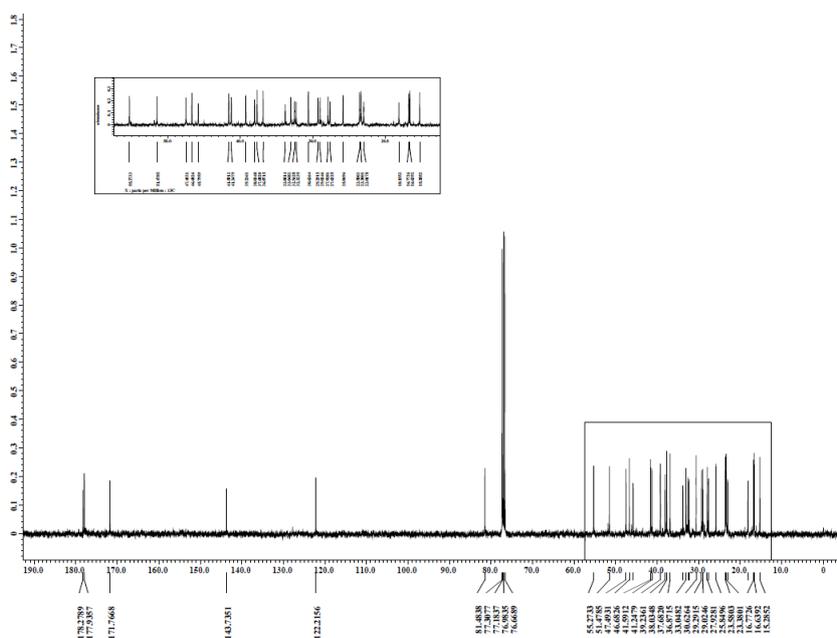
1) ESI-MS (-) Spectra of compound **4**



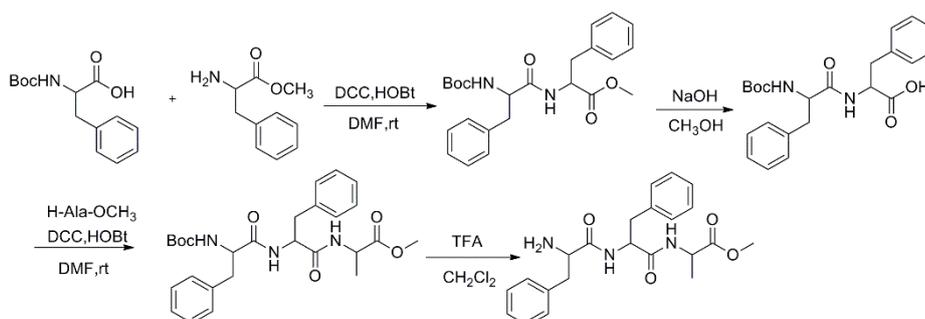
2) ^1H NMR Spectra of compound **4** (CDCl_3 , 400MHz)



3) ^{13}C NMR Spectra of compound **4** (CDCl_3 , 100MHz)

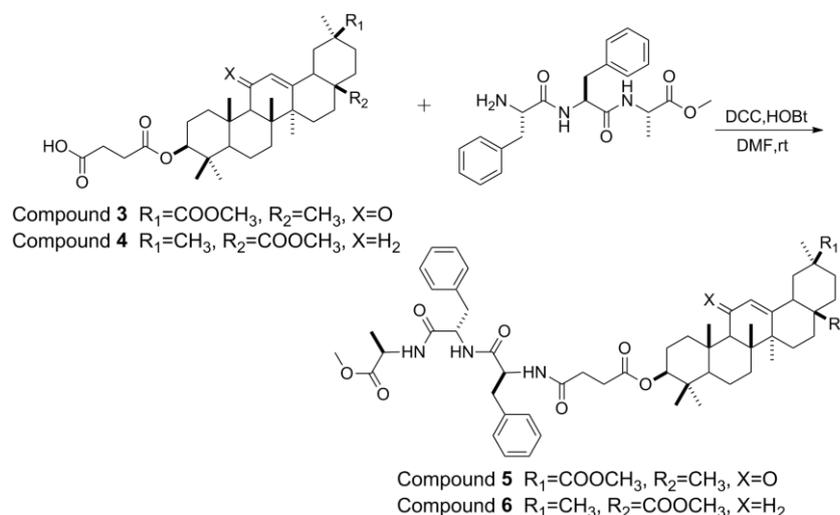


2. Synthesis of $\text{NH}_2\text{-Phe-Phe-Ala-OMe}$



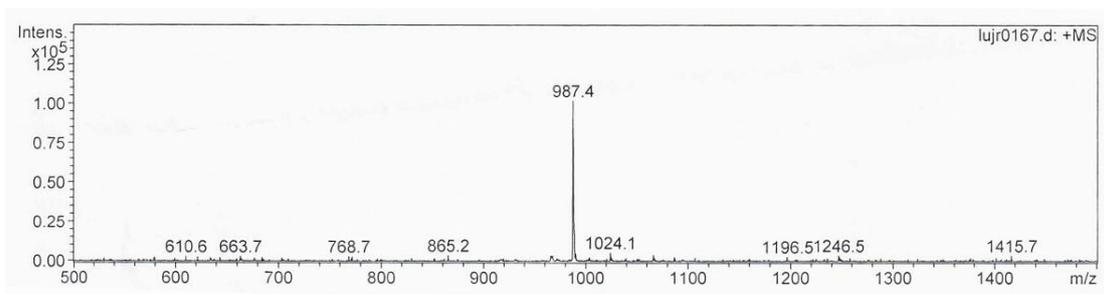
The peptide was synthesized as described by the reference.¹

3. Synthesis of compound **5** and **6**

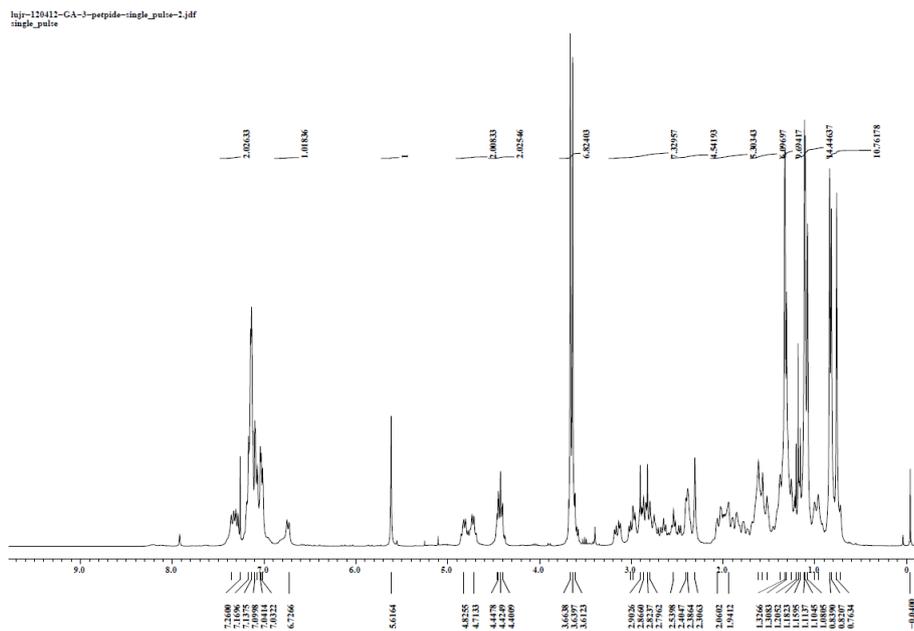


657 mg (1.13 mmol) **3** was dissolved in 20 ml DMF solvent and cooled in ice bath. 450 mg (1.13mmol) NH_2 -Phe-Phe-Ala-OMe was added to the reaction mixture followed by DCC (232 mg, 1.13 mmol) and HOBT (155 mg, 1.13 mmol). The reaction mixture was stirred for 24h. The reaction mixture was filtered and the solids were washed with ethyl acetate. After evaporating the solvents under vacuum the residues were dissolved with ethyl acetate. The solution was washed with HCl (2M) (3×50 mL), brine (2×50 mL), and then dried over anhydrous sodium sulfate and evaporated in vacuum to yield solid. Purification was done by silica gel column (100–200 mesh) using CH_2Cl_2 : CH_3OH = 60:1 as eluent to give **5** as a white solid (560 mg, 51%). ESI-MS m/z : 987.4 $[M+Na]^+$, 1024.1 $[M+K]^+$, 999.8 $[M+Cl]^-$. 1H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.36~7.29(2d, 2H, -NH) 7.17~7.01 (m, 10H, Phe-benzene), 6.65(d, $J=7.56$ Hz, 1H, -NH) 6.73(d, $J=6.87$ Hz, 1H, -NH) 5.61(s, 1H, 12-H) 4.83~4.71, 4.46~4.40 (m, 4H, α -H, 3-H) 3.69, 3.60 (2s, 6H, 2- $COOCH_3$), 1.11, 0.91, 0.91, 0.88, 0.83, 0.83, 0.70(7×s, 7×3H,23,24,24,26,27,29,30- CH_3) ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 200.16(11-C), 177.01, 173.23, 172.91, 172.22, 171.00, 170.80, 169.60, 137.07, 136.40, 129.29, 129.23, 128.65, 128.45, 126.99, 126.74, 81.71, 61.69, 55.00, 54.52, 54.26, 52.42, 51.84, 48.46, 48.19, 45.46, 44.10, 43.31, 41.14, 38.77, 38.09, 37.98, 32.65, 31.90, 31.18, 30.97, 29.84, 28.60, 28.37, 28.13, 26.46, 23.61, 23.49, 18.73, 18.49, 17.96,17.42, 16.82, 16.49

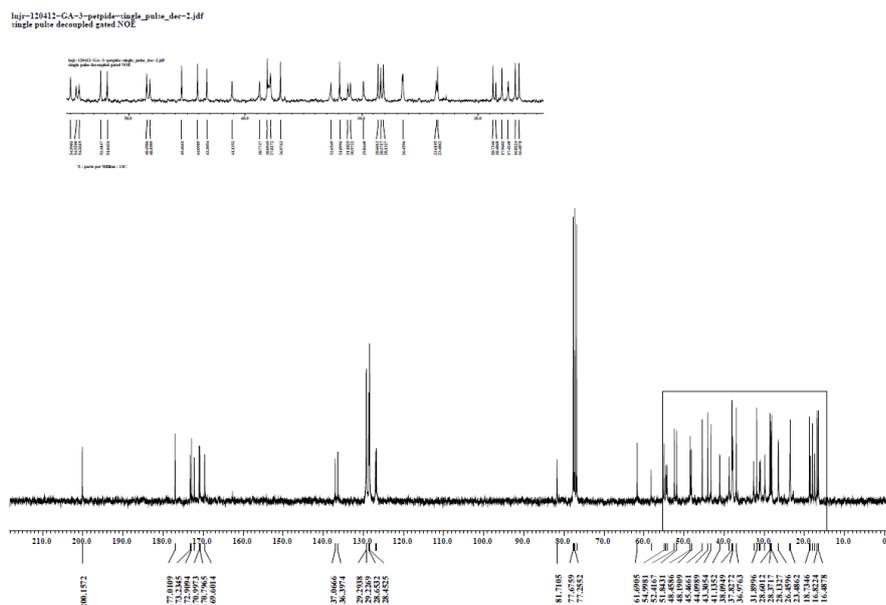
1) ESI-MS (+) Spectra of compound **5**



2) ¹H NMR Spectra of compound **5** (CDCl₃, 300MHz)



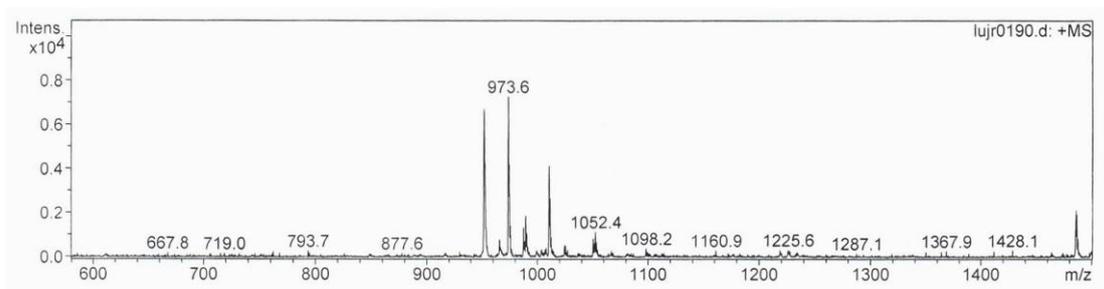
3) ¹³C NMR Spectra of compound **5** (CDCl₃, 75MHz)



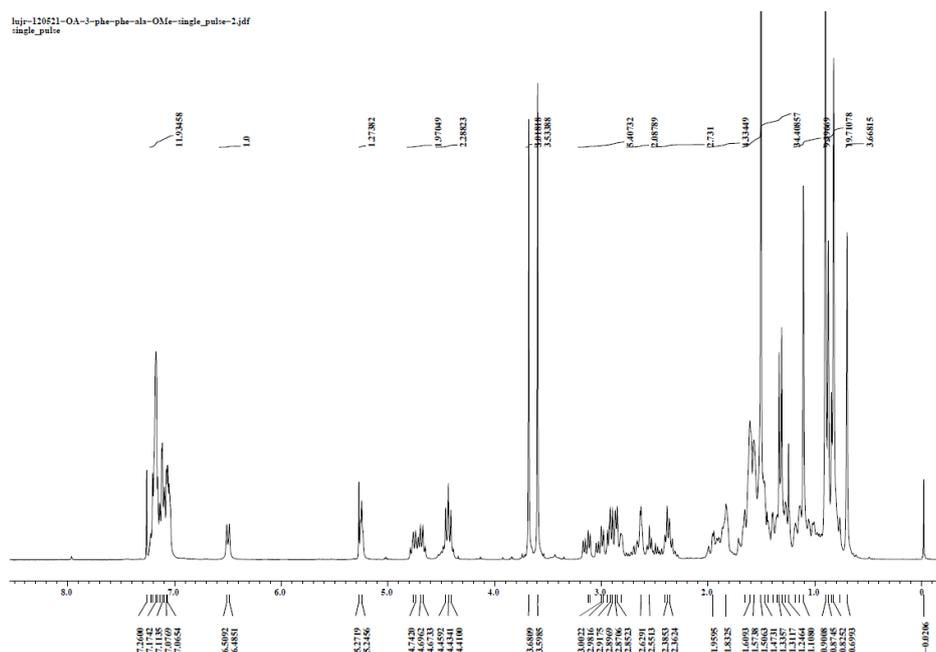
The compound **6** was synthesized by using the same procedure as that described for **5**.
ESI-MS m/z : 951.8 [M+H]⁺, 973.6 [M+Na]⁺, 989.4 [M+K]⁺ ¹H NMR (CDCl₃, 300 MHz, δ ppm):

7.22~6.96 (m, 12H, phe-benzene and 2-NH), 6.35(d, J=7.20 Hz, 1H, -NH) 6.73(d, J=6.87 Hz, 1H, -NH) 5.25(s, 1H, 12-H) 4.75~4.64, 4.46~4.42 (m, 4H, α -H, 3-H) 3.66, 3.64 (2s, 6H, 2-COOCH₃), 1.33, 1.11, 1.10, 1.08, 0.84, 0.82, 0.76 (7 \times s, 7 \times 3H, 23,24,24,26,27,28,29-CH₃) ¹³C NMR (CDCl₃, 75 MHz, δ ppm): 178.36, 173.16, 172.84, 172.14, 170.92, 172.58, 143.92, 137.00, 136.34, 12.29, 129.24, 128.72, 128.51, 127.05, 126.82, 122.24, 81.99, 55.33, 54.54, 54.39, 52.43, 51.58, 48.20, 47.58, 46.79, 45.93, 41.74, 41.37, 39.35, 38.13, 37.88, 37.77, 37.00, 33.93, 33.17, 32.61, 32.45, 31.02, 30.75, 29.81, 28.16, 27.76, 27.49, 26.03, 23.72, 23.58, 23.47, 23.14, 18.28, 18.01, 16.91, 16.82, 15.41

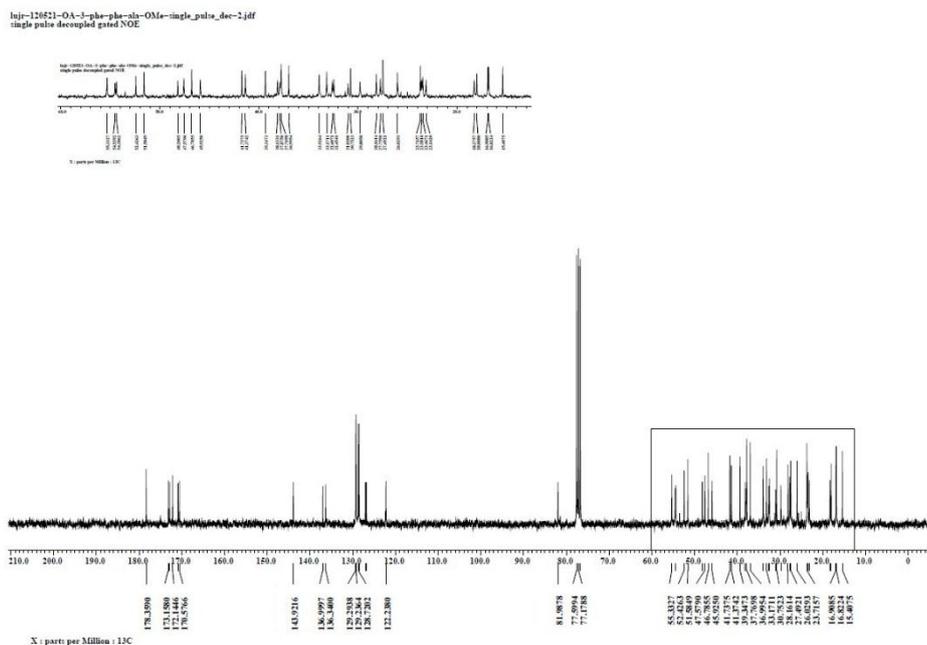
1) ESI-MS (+) Spectra of compound **6**



2) ¹H NMR Spectra of compound **6**(CDCl₃, 300MHz)



3) ¹³C NMR Spectra of compound **6**(CDCl₃, 75MHz)



4. The Photographs of gel formation in organic solvents.

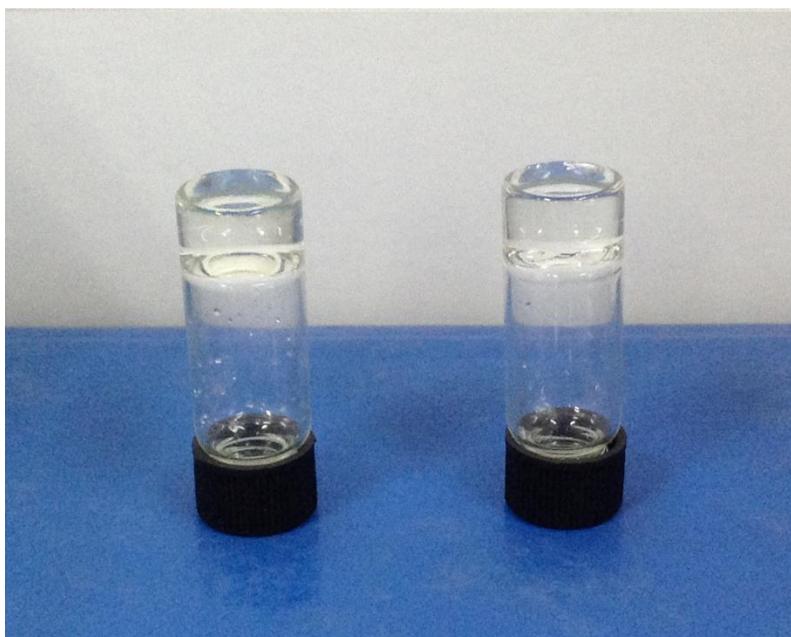


Figure S1. Gels containing **6** in (left) benzene (2.0g/100cm³) and (right) toluene (1.8g/100cm³)

5. The lamellar morphology observed by SEM images

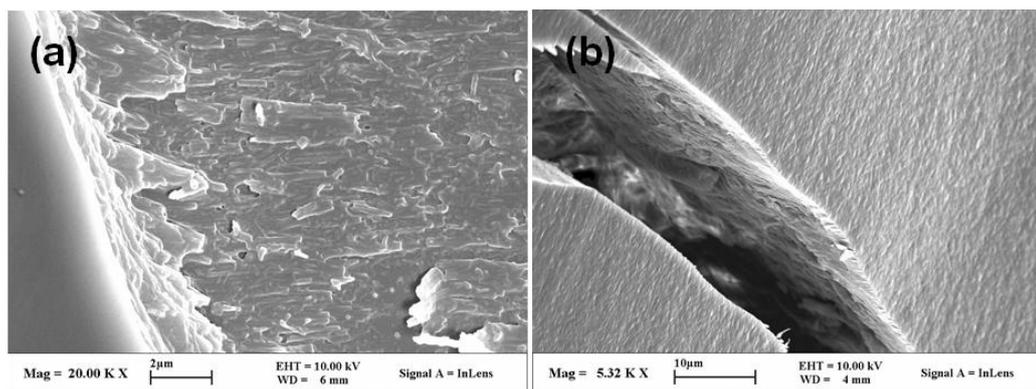


Figure S2. A lamellar morphology observed from the dried gel of **5** (a) and **6** (b) in O-xylene by SEM.

6. XRD patterns of xerogel **5** and **6** from toluene

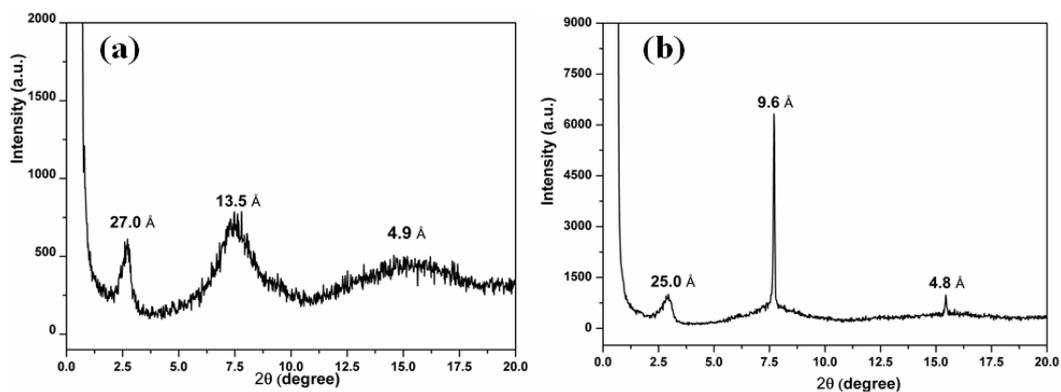


Figure S3. XRD patterns of xerogel **5** and **6** from toluene

7. IR spectra of **5** in solution, IR spectra of **6** in solid and xerogel

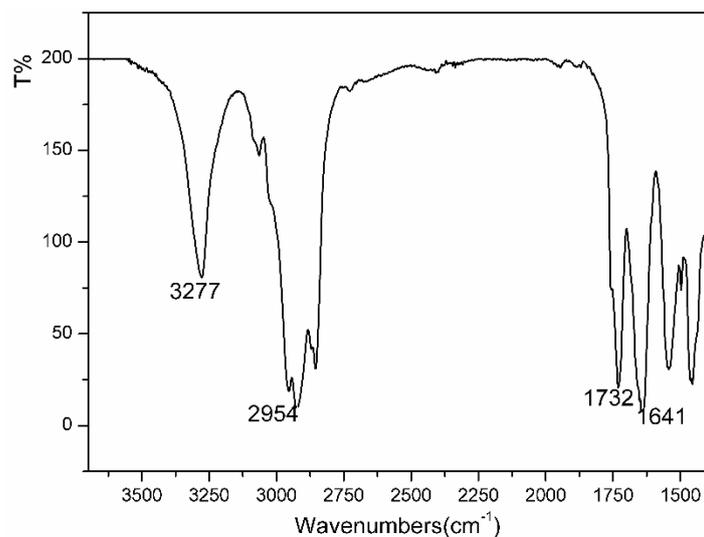


Figure S4. IR spectra of **5** in CHCl₃ solution

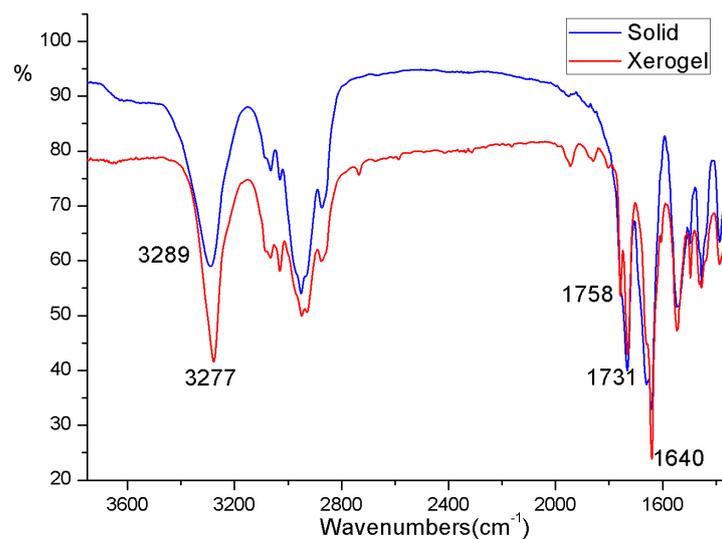


Figure S5. IR spectra of **6** in solid and xerogel (1.0 g/100 cm³) made from toluene

8. Selective gelation of toluene layer

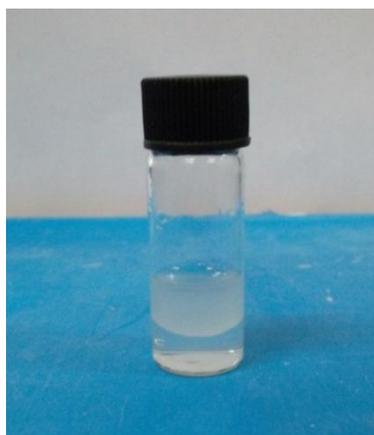


Figure S6. Selective gelation of toluene layer by **6** from water at rt.

9. Dye solution interacted with solid **6**

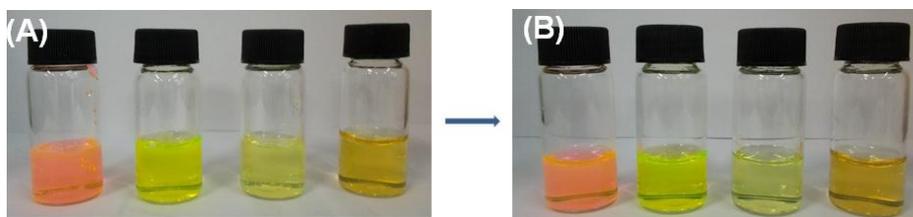


Fig. S7 (A) Photograph of solid **6** in the dye solution of (from left to right: Rhodamine 6G, Fluorescein disodium, Acriflavine, Cresol red) (B) Photograph of dye solution after interaction with solid **6** for 24h.