

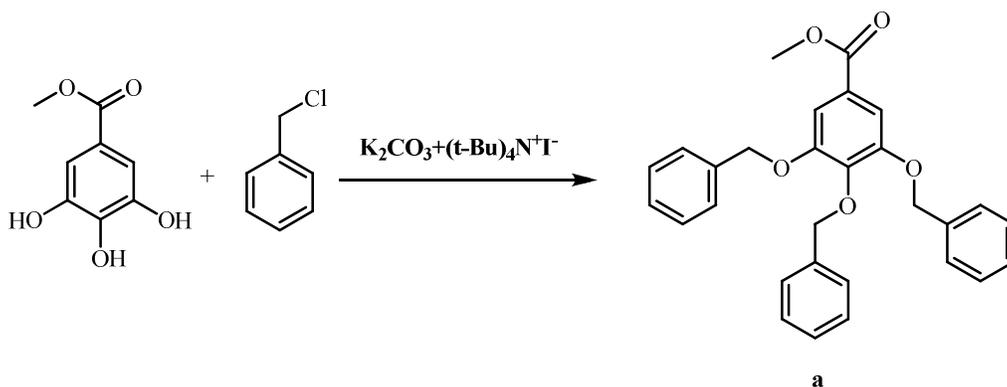
Glucose Cored Poly(Aryl Ether) Dendron based Low Molecular Weight Gels: pH Controlled Morphology and Hybrid Hydrogel Formation

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1. Synthetic Procedures and Characterization of Dendrons

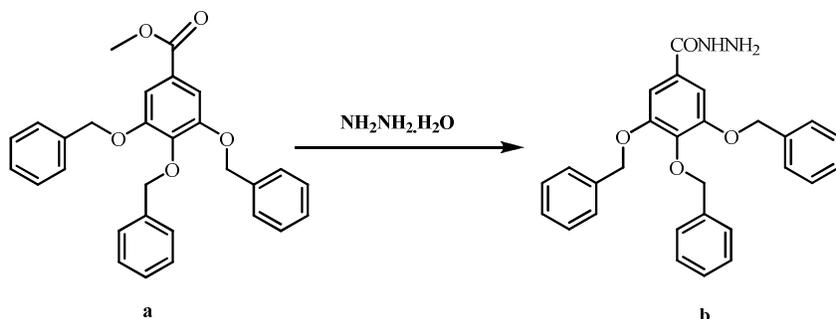
1.2. Synthetic Procedure for Compound I

1.2.1. Synthesis of Compound a



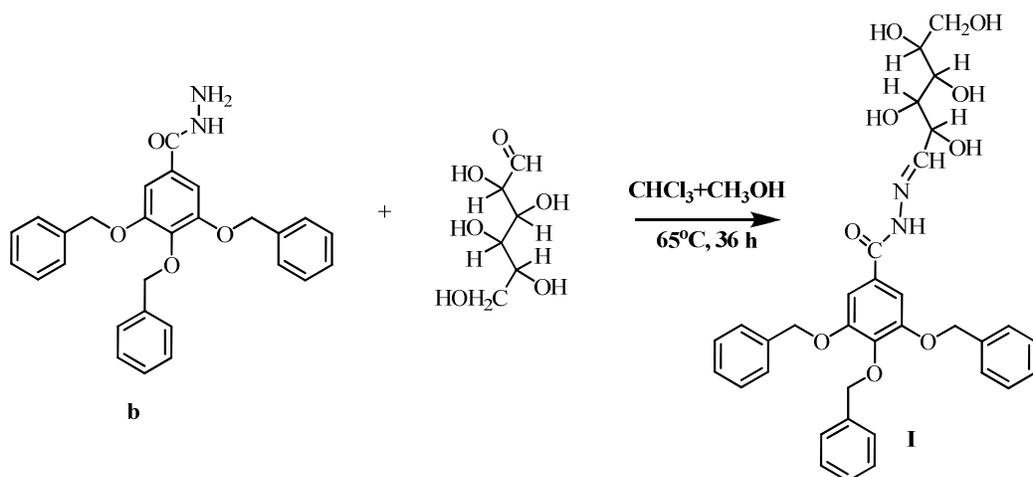
Methyl-3, 4, 5-trihydroxybenzoate (9 g, 0.045 mole) and potassium carbonate (24.84 g, 0.18 mole) were taken in 130 mL of 1,4-dioxane in a 250 mL round bottom flask. Benzyl chloride (33 mL, 0.135 mole) was added to the above reaction mixture, followed by the addition of a catalytic amount of tetra butyl ammonium iodide (1.4 g, 0.0045 mole). The solution was heated to refluxing condition along with stirring for 24 hours. The solvent was then removed under reduced pressure using a rotary evaporator, affording an oily substance, which turned into a solid upon standing. The solid was recrystallized from methanol to yield the product (compound **a**)(18.5 g, 90.5%); 1H NMR (400 MHz, $CDCl_3$) δ : 3.8 (s, $COOCH_3$, 3H), 4.9 (s, $ArCH_2O$, 2H), 5.01 (s, $ArCH_2O$, 4H), 7.1-7.3 (m, ArH & PhH , 17H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 52.25, 71.27, 75.15, 109.13, 125.26, 127.57, 127.96, 128.04, 128.21, 128.56, 136.69, 137.48, 142.46, 152.59, 166.66; IR (KBr) ν = 3064, 3031, 2947, 2878, 1715, 1589, 1499, 1453, 1110 and 754 cm^{-1} .

1.2.2. Synthesis of G₁TNHNH₂ (b)



Compound **a** (4 g, 0.0088 mole) and hydrazine monohydrate (22 mL, 0.44 mole) were dissolved in MeOH (30 mL) and THF (15 mL). The reaction mixture was stirred at 70 °C for 12 hours. After the heating was stopped, the reaction mixture was allowed to cool to room temperature, and the volatiles were removed under reduced pressure. The residue was dissolved in CH₂Cl₂ and washed with H₂O. The organic layer was then dried over anhydrous Na₂SO₄, and the solvent was evaporated to get crude product, which was purified by column chromatography using silica gel as the stationary phase and 5% MeOH in CH₂Cl₂ as the eluent to get the pure product (**b**) as a white powder (3.75 g, 93 %); ¹H NMR (400 MHz, CDCl₃) δ: 5.03 (s, ArCH₂O, 6H), 6.96 (s, ArH, 2H), 7.18-7.30 (m, PhH, 15H); ¹³C NMR (100 MHz, CDCl₃) δ: 71.54, 75.31, 106.96, 127.60, 128.09, 128.19, 128.32, 128.69, 136.70, 137.52, 141.72, 142.57, 153.03, 168.44; IR(KBr)_v = 3282, 3195, 3110, 3089, 3063, 3030, 3007, 2940, 2870, 1631, 1583, 1518, 1498, 1455, 1423, 1153 and 779 cm⁻¹; HRMS (ES⁺): *m/z* Calcd for C₂₄H₂₆N₂O₄: 454.1893, found: 455.1964[M+H]⁺; m.p. 122 °C.

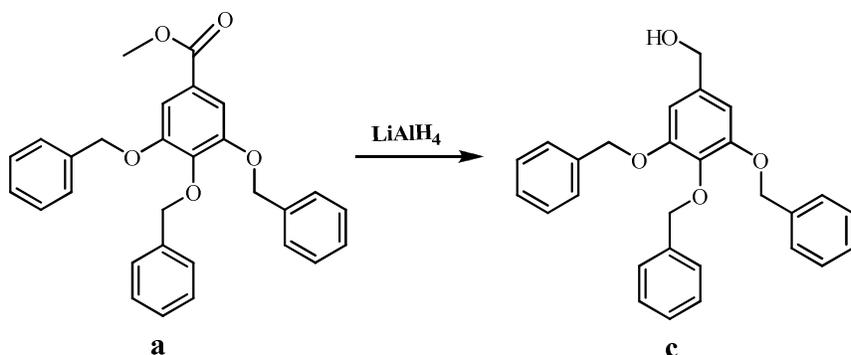
1.2.3.Synthesis of Compound I



Compound **b** (2 g, 0.0044 moles) and glucose (1.0305 g, 0.0057 moles) was dissolved in 50ml CHCl_3 -MeOH (1:3 v/v) mixture. The mixture was stirred at 65°C for 36 hours. The compound was purified by column chromatography using silica gel as the stationary phase and 15%MeOH in CHCl_3 as the eluent to get the pure product (**c**) as a white solid (2.3 g, 85%). ^1H NMR (500 MHz, DMSO-d_6) δ : 3.03 (m, OH, CH, 2H), 3.15 (m, OH, 1H), 3.23 (m, CH, 1H), 3.46 (m, CH, 1H), 3.70 (m, OH, 1H), 3.85 (d, OH, 1H), 4.31 (q, $j = 4.5$ OH, 1H), 4.92 (m, CH, 2H), 4.99 (s, CH_2 , 2H), 5.17 (s, CH_2 , 4H), 5.23 (s, CH, 1H), 5.89 (s, $\text{CH}=\text{N}$, 1H), 7.26-7.41 (m, ArH & PhH, 17H), 10.05 (s, CONH, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ : 61.18, 70.15, 70.23, 71.14, 74.11, 76.54, 78.10, 91.09, 106.39, 127.57, 127.97, 128.34, 136.76, 137.33, 139.61, 151.87, 165.51; HRMS (ES+): m/z Calcd for $\text{C}_{34}\text{H}_{36}\text{N}_2\text{O}_9$: 616.2421 found: 639.2327 $[\text{M}+\text{Na}]^+$.

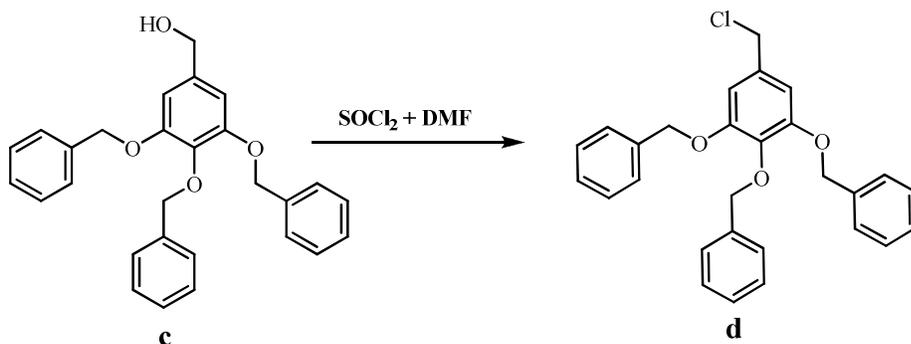
1.3. Synthetic Procedure for Compound II

1.3.1. Synthesis of Compound c



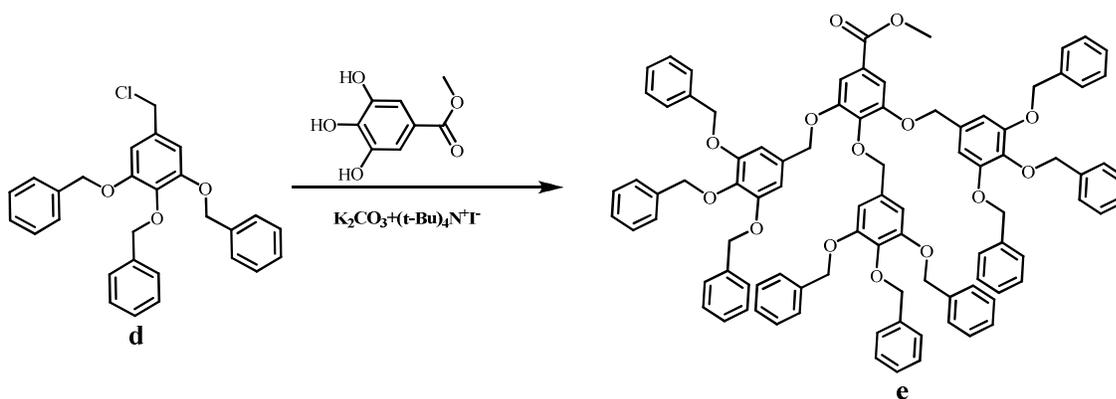
Lithium aluminum hydride (0.809 g, 0.0213 mole) was suspended in 40 mL of freshly distilled THF in a dry three-neck round-bottom flask under nitrogen atm. Compound **a** (9 g, 0.0198 mole) was dissolved in 50 mL of freshly distilled THF and added drop wise to the lithium aluminum hydride solution. The reaction mixture was refluxed with stirring for 2 h. The THF solution was cooled to room temperature and transferred to a beaker. Water was added drop wise to the vigorously stirred THF solution until the gray color of the lithium aluminum hydride was disappeared and a white solid was formed which is filtered and washed with THF. Excess solvent was removed under reduced pressure and the crude product was recrystallized from 95% methanol/water mixture to get the pure product (**c**) (7.6 g, 90%); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 4.6 (s, CH_2OH , 2H), 5.09 (s, ArCH_2O , 2H), 5.15 (s, ArCH_2O , 4H), 6.72 (s, ArH , 2H), 7.30-7.48 (m, PhH , 15H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 65.42, 71.22, 75.26, 106.46, 127.45, 127.83, 127.90, 128.18, 128.52, 128.62, 136.66, 137.13, 137.81, 137.87, 153.02.

1.3.2. Synthesis of [(AB)₃G₁-Cl] (d)



To a solution of **c** (5 g, 0.0117 mole) in dichloromethane (40 mL) was added a catalytic amount of DMF (3 mL) followed by SOCl₂ (1.6 mL, 0.014 mole) with stirring. The reaction mixture was stirred at room temperature for 2 hours. The solvent and excess SOCl₂ were distilled out under reduced pressure. The resulting yellow solid was dissolved in diethyl ether and washed with water and the organic layer was dried over Na₂SO₄. The solvent was removed under reduced pressure and directly used for further step.

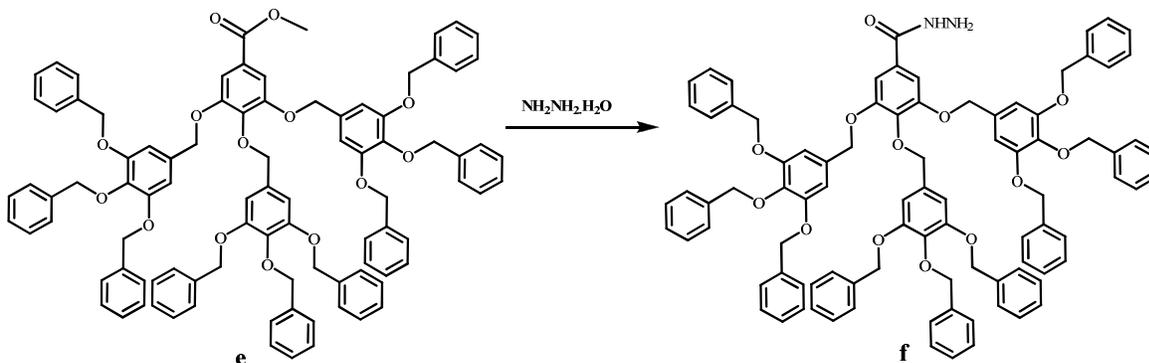
1.3.3. Synthesis of (AB)₃G₂-COOCH₃ Dendron (e)



Methyl-3, 4, 5- trihydroxy benzoate (0.61 g, 0.0034 mole) and K₂CO₃ (3.31 g, 0.0204 mole) in 35 mL dry acetone were taken in a 100 mL round bottom flask. Compound **d** (4.5 g, 0.010 mole) was added followed by the addition of a catalytic amount of tetra butyl ammonium iodide (0.365 g, 0.001 mole). The solution was heated to reflux with stirring for 24 hours. After completion of reaction, the reaction mixture was cooled to room temperature and filtered. The filtered salts were further washed twice with dichloromethane. The solvent was then removed under reduced

pressure using a rotary evaporator, yielding an oily substance that turned into a solid upon standing. The solid was recrystallized from hexane: toluene mixture (70:30). The yield of the product (compound **e**) was 4.2 g (89.3%); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 3.82 (s, COOCH_3 , 3H), 4.75-4.93 (s, ArCH_2O , 24H), 6.66 (s, ArH , 2H), 6.68 (s, ArH , 4H), 7.10-7.29 (m, ArH & PhH , 47H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 52.31, 71.03, 71.25, 71.49, 75.10, 75.21, 107.03, 107.65, 109.71, 125.44, 127.45, 127.49, 127.67, 127.77, 127.88, 128.10, 128.16, 128.40, 128.49, 132.29, 133.06, 136.99, 137.03, 137.92, 138.30, 142.43, 152.51, 152.83, 153.11, 166.51; $\text{IR}(\text{KBr})\nu = 3088, 3062, 3030, 2934, 2864, 1719, 1591, 1504, 1454, 1435, 1112$ and 733 cm^{-1} .

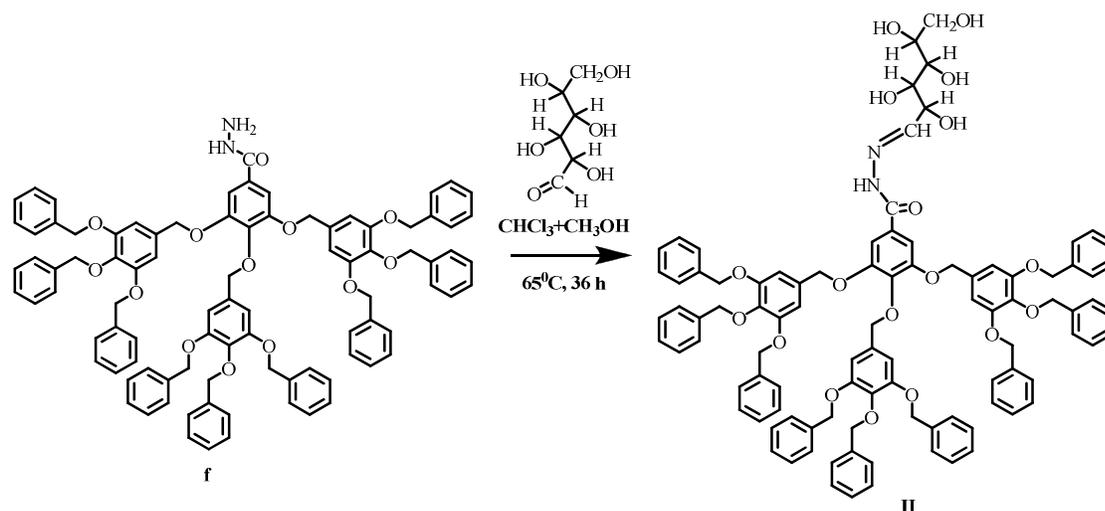
1.3.4. Synthesis of G_2TNHNH_2 (**f**)



Compound **e** (3 g, 0.0021 mole) and hydrazine monohydrate (5.3 mL, 0.11 mole) were placed in a round bottomed flask and dissolved in MeOH (20 mL) and THF (20 mL). The reaction mixture was stirred at 70°C for 12 hours. The heating was stopped, the reaction mixture was allowed to cool to room temperature, the volatiles were removed under reduced pressure, and the product was dissolved in CH_2Cl_2 and washed with H_2O . The organic layer was dried over anhydrous Na_2SO_4 , and the solvent was evaporated to get crude product, which was purified by column chromatography by using silica gel as the stationary phase and 5% MeOH in CH_2Cl_2 as the eluent to get the pure product (compound **f**) as a white powder (2.71 g, 93.3%); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 4.73-4.89 (m, ArCH_2O , 24H), 6.63-6.65 (m, ArH , 6H), 6.94 (s, ArH , 2H), 7.13-7.32 (m, PhH , 45H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 71.05, 71.25, 71.63, 75.19, 75.26, 106.91, 107.28, 107.61, 127.51, 127.73, 127.83, 127.94, 128.16, 128.21, 128.45, 128.55, 132.24, 133.08, 136.98, 137.03, 137.91, 138.31, 141.53, 152.90, 153.15, 168.13; $\text{IR}(\text{KBr})\nu = 3286, 3109, 3088,$

3062, 3030, 2932, 2865, 1637, 1590, 1505, 1454, 1435, 1121 and 733 cm^{-1} ; **HRMS (ES+)**: m/z
Calcd for $\text{C}_{91}\text{H}_{80}\text{N}_2\text{O}_{13}$: 1408.5660, found: 1410.5817; m.p. 120 °C.

1.3.3. Synthesis of Compound II



Compound **f** (1.0536 g, 0.000754 moles) and Glucose (0.202 g, .00112 moles) was dissolved in 50ml CHCl_3 -MeOH (1:3 v/v) mixture. The mixture was stirred at 65°C for 36 hours. Compound was purified by column chromatography using silica gel as the stationary phase and 15% MeOH in CHCl_3 as the eluent to get the pure product as a white solid **II** (0.9950 g, 89%); **^1H NMR (400 MHz, CDCl_3)** δ : 2.04 (m, OH, CH, 3H), 3.28 (m, OH, 1H), 3.46 (m, CH, 5H), 3.69 (m, CH, 1H), 4.57-5.00 (s, CH_2 , 24H), 5.52 (s, $\text{CH}=\text{N}$, 1H), 6.65 (m, CH, 6H), 7.26-7.41 (m, ArH & PhH, 47H), 9.12 (s, CONH, 1H); **^{13}C NMR (125 MHz, DMSO-d_6)** δ : 61.18, 69.87, 70.08, 70.23, 70.74, 71.14, 74.15, 74.24, 76.66, 78.21, 91.26, 106.25, 106.51, 127.41, 127.52, 127.56, 127.58, 127.65, 127.70, 127.91, 127.96, 128.19, 128.22, 128.25, 128.29, 132.57, 133.58, 136.73, 136.82, 137.65, 140.15, 152.03, 152.25, 165.56; **HRMS (ES+)**: m/z Calcd for $\text{C}_{97}\text{H}_{90}\text{N}_2\text{O}_{18}$: 1570.6189 found: 639.2327 $[\text{M}+\text{Na}]^+$.

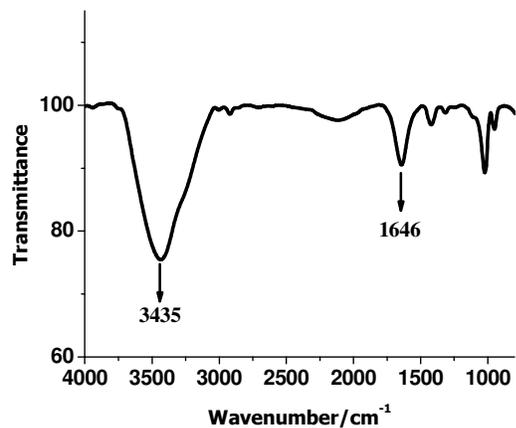


Fig. S1 FT-IR spectrum of xerogel formed from compound **I**

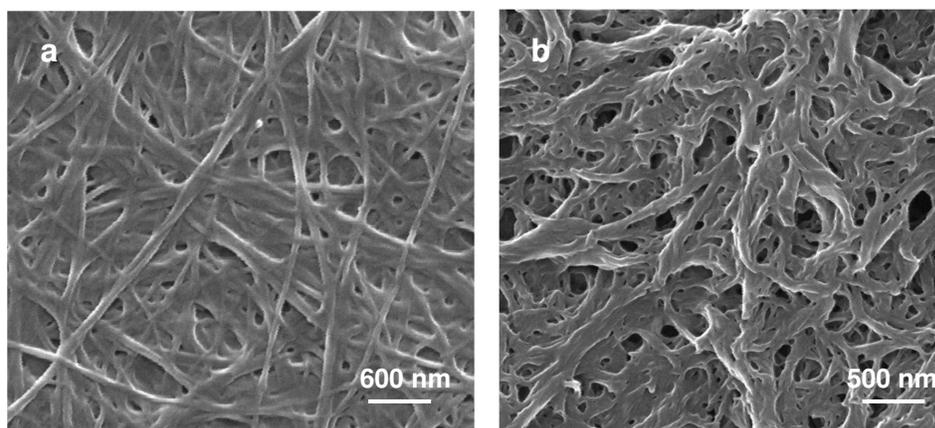


Fig. S2 SEM image of xerogel a) compound **I** from DMSO-water b) compound **II** from MeOH.

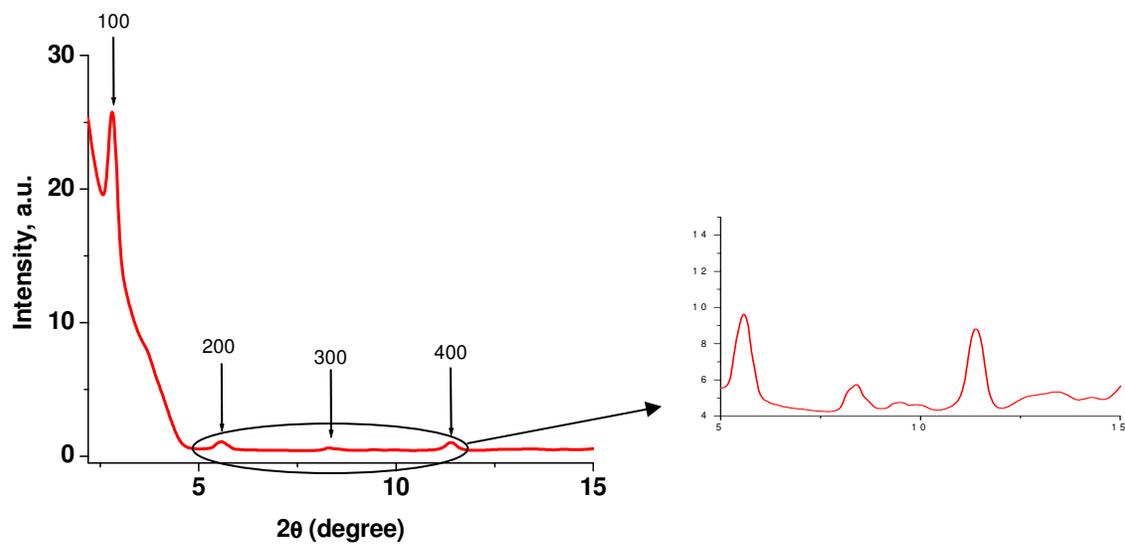


Fig. S3 Powder XRD pattern of xerogel formed compound **I** in DMSO-water.

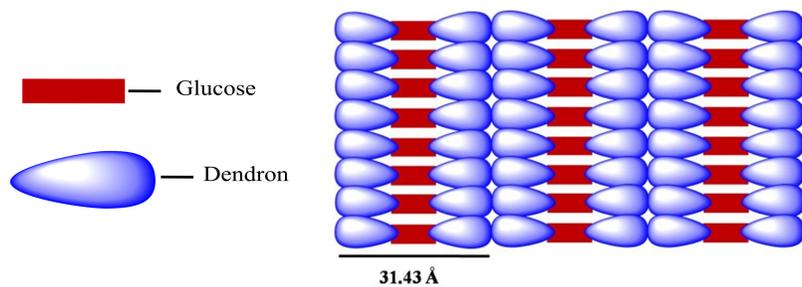


Figure S4: Schematic representation of the molecular arrangement in the gel.

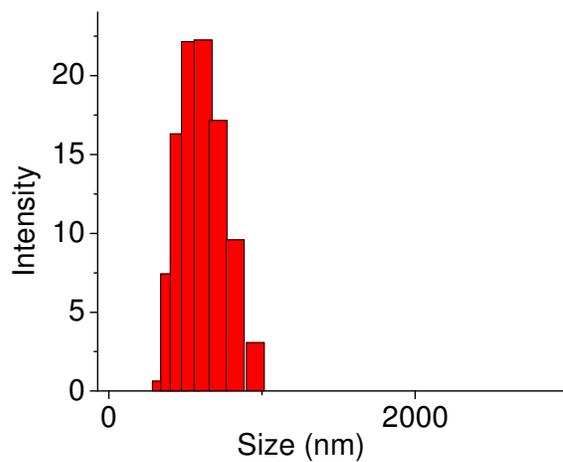


Fig. S5 DLS histogram of compound **I** in DMSO-water (1:9) in pH =10

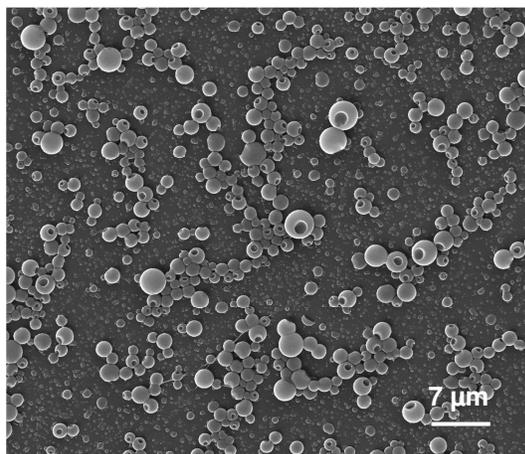


Fig. S6 SEM image of compound **I** in DMSO-water in pH=10



Fig. S7 Photograph of gel in the presence of graphene oxide.