Supporting information

Metal induced Gelation from Pyridine Cored Poly(Aryl Ether) Dendron with In-situ Synthesis and Stabilization of Hybrid Hydrogel Composite

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General information

The poly(aryl ether) dendron derivatives have been synthesized according to reported procedures. All the starting materials were obtained from Sigma–Aldrich or s.d. fine-chem. Pvt. Ltd. India. The used organic solvents were dried according to standard procedures. $^1$H and $^{13}$C NMR data were collected on a Bruker 400 MHz and 500 MHz spectrometer ($^1$H: 400 MHz; $^1$H: 500 MHz; $^{13}$C: 100 MHz). Mass spectra were recorded using Micromass Q-TOF mass spectrometer and Voyager-DE PRO MALDI/TOF mass spectrometer with α-cyano-4-hydroxycinnamic acid (CCA) as the matrix. IR spectrum was recorded using Jasco FT/IR-4100 spectrometer. The UV-Vis spectroscopic studies were carried Jasco V-660 Spectrophotometer. The scanning electron microscopic studies were carried out using a FEI-Quanta Microscope. Powder- XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation ($\lambda = 1.54178$ Å). Rheological studies were conducted in Anton Paar Rheometer MCR-301. X-ray photoelectron spectroscopy (XPS) measurement are performed with an Omicron ESCA Probe spectrometer with polychromatic Mg-Kα X-rays ($h\nu = 1253.6$ eV). Gel Preparation: The 1 eq of dendron (1) (0.25 wt% ) was dissolved in 1 mL of THF and 0.5 eq silver nitrate was dissolved in water (1 mL). Silver nitrate solution was mixed with dendron solution and silver nitrate solution was added, followed by sonication for few second leads to the formation of opaque gels that did not flow under tube inversion.
Synthetic procedures and characterization of dendrons

Synthetic procedure for compound I

Synthesis of \((AB)_3\) \(G_1\)-COOCH\(_3\) (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%); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 3.8 (s, COOCH\(_3\), 3H), 4.9 (s, ArCH\(_2\)O, 2H), 5.01 (s, ArCH\(_2\)O, 4H), 7.1-7.3 (m, ArH&PhH, 17H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 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) \(\nu = 3064, 3031, 2947, 2878, 1715, 1589, 1499, 1453, 1110\) and 754 cm\(^{-1}\).

Synthesis of \(G_1\)TNHNH\(_2\) (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 CH\(_2\)Cl\(_2\)
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 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) ν =3282, 3195, 3110, 3089, 3063, 3030, 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.

**Synthesis of compound I**

A solution of 4-pyridine carboxaldehyde (0.497ml, 5.28 mmole) in methanol was added drop wise to a CHCl₃ solution of compound b (2 g, 4.40 mmole). The mixture was stirred for 1 hour and the resulting gel was dried under vacuum to yield I (2.368 g, 99%). ¹H NMR (400 MHz, CDCl₃) δ: 4.97(s, ArCH₂O, 4H), 5.01(s, ArCH₂O, 2H), 7.06 (s, ArH, 2H), 7.16-7.27 (m, PhH, 15H), 7.43 (s, PyH, 2H), 8.14 (s, CONH, 1H), 8.54 (s, PyH, 2H), 10.01(s, CH=N, 1H); ¹³C NMR (125 MHz, CDCl₃,DMSO-d₆) δ: 71.26,75.02, 107.04, 121.22, 127.51,127.90, 128.00, 128.12, 128.35, 128.40, 128.42, 128.47, 128.50, 128.52, 128.57, 136.51, 137.31, 141.64, 145.58, 150.14, 152.53, 164.18; HRMS (ES⁺): m/z Calcd for C₃₄H₂₉N₃O₄: 543.2158, found: 544.2215 [M+H]⁺.
Synthetic procedure for compound II

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 Compound c (7.6 g, 90%); $^1$H NMR (400 MHz,
CDCl$_3$ $\delta$: 4.6 (s, CH$_2$OH, 2H), 5.09 (s, ArCH$_2$O, 2H), 5.15 (s, ArCH$_2$O, 4H), 6.72 (s, ArH, 2H), 7.30-7.48 (m, PhH, 15H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 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.

Synthesis of [(AB)$_3$G$_1$-Cl] (d)

To a solution of compound c (5 g, 0.0117 mole) in dichloromethane (40 mL) was added a catalytic amount of DMF (3 mL) followed by SOCl$_2$ (1.6 mL, 0.014 mole) with stirring. The reaction mixture was stirred at room temperature for 2 hours. The solvent and excess SOCl$_2$ 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 Na$_2$SO$_4$. The solvent was removed under reduced pressure and directly used for further step.

Synthesis of (AB)$_3$G$_2$-COOCH$_3$ dendron (e)

Methyl-3, 4, 5- trihydroxy benzoate (0.61 g, 0.0034 mole) and K$_2$CO$_3$ (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%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 3.82 (s, COOC$_3$H$_7$, 3H), 4.75-4.93 (s, ArCH$_2$O, 24H), 6.66 (s, ArH, 2H) 6.68 (s, ArH, 4H), 7.10-7.29 (m, ArH&PhH, 47H);$^{13}$C NMR(100 MHz, CDCl$_3$) $\delta$: 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; IR (KBr) $\nu$ = 3088, 3062, 3030, 2934, 2864, 1719, 1591, 1504, 1454, 1435, 1112 and 733 cm$^{-1}$. 
Synthesis of G\textsubscript{2}TNHNH\textsubscript{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\textsubscript{2}Cl\textsubscript{2} and washed with H\textsubscript{2}O. The organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{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\textsubscript{2}Cl\textsubscript{2} as the eluent to get the pure product as a white powder (2.71 g, 93.3 %); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 4.73-4.89 (m, ArCH\textsubscript{2}O, 24H), 6.63-6.65 (m, ArH, 6H), 6.94 (s, ArH, 2H), 7.13-7.32 (m, PhH, 45H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 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; IR(KBr) \(v\)=3286, 3109, 3088, 3062, 3030, 2932, 2865, 1637, 1590, 1505, 1454, 1435, 1121 and 733 cm\textsuperscript{-1}; HRMS (ES\textsuperscript{+}): m/z Calcd for C\textsubscript{91}H\textsubscript{80}N\textsubscript{2}O\textsubscript{13}: 1408.5660, found: 1410.5817; m.p. 120 °C.

Synthesis of compound II

A solution 4-pyridine carboxaldehyde (0.16 ml, 1.703 mmole) in methanol was added drop wise to a CHCl\textsubscript{3} solution of compound f (2 g, 1.418 mmole) under nitrogen atmosphere. The mixture was stirred for 1 hour and the resulting gel was dried under vacuum to yield II (1.998 g, 94 %); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 5.19 (s, ArCH\textsubscript{2}O, 4H), 6.95 (s, ArH, 1H), 7.26-7.49 (m, ArH&PhH, 12H), 8.06 (dd, J=8.0 Hz, J=3.6 Hz, PyH, 2H), 8.49 (s, PyH, H), 8.93 (d, J=6.0 Hz, PyH, 2H), 9.39 (s, CH=N, 1H); \textsuperscript{13}C NMR (100 MHz, DMSO-d\textsubscript{6}) \(\delta\): 70.61, 70.82, 71.16, 74.88, 74.93, 106.98, 107.57,107. 61, 108. 74, 127.15, 127.55, 127.74, 128.13, 128.31, 128.46, 128.63,128.88, 128.95, 128.98, 130.24, 130.78, 131.12, 131.30, 131.77, 131.89, 133.84, 133.98, 134.80, 134.93, 137.25, 137.41, 148.36, 151.90, 152.54, 168.29; MS (MALDI-TOF): m/z Calcd for C\textsubscript{91}H\textsubscript{83}N\textsubscript{3}O\textsubscript{13}: 1497.5926; found: 1520.6752 [M+Na]\textsuperscript{+}. 
**Fig. S1** FT-IR spectrum of the xerogel formed from compound I/AgNO₃ (1:0.5 eq) in THF-water
Fig. S2 Schematic representation of lamellar arrangement

Fig. S3 Powder-XRD pattern of copper complex gel from compound I/Cu (OAc)$_2$ (1:0.5 eq) in THF-water
**Fig. S4** UV-vis absorption spectrum of the silver nanoparticles obtained from I-Ag and corresponding dendron solution.

**Fig. S5** Powder X-ray diffraction pattern for gel fiber embedded silver nanoparticle.
**Fig. S6** TEM image of gel fiber embedded nanoparticle of I-Ag.

**Fig. S7** EDAX spectrum of gel fiber embedded nanoparticle of I-Ag.
**Fig. S8** X-Ray photoelectron spectroscopy of gel fiber embedded nanoparticles of I-Ag

**Reference**