Design, synthesis and gelation studies of 4,6-*O*-butylidene-α,β-unsaturated-β-*C*-glycosidic ketones: application to plant tissue culture†

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A series of α,β-unsaturated-β-*C*-glycosidic ketones was synthesized starting from D-glucose in three steps. 4,6-*O*-Butylidene-β-*C*-glycosidic ketones on aldol condensation with aromatic and heteroaromatic aldehydes in the presence of a suitable organocatalyst led to the stereoselective formation of the products in good yield. Hydrogen bonding and π–π stacking of these derivatives were established by single-crystal XRD. The soft material derived from this method had a diameter of 10–200 nm with a three-dimensional network, as determined by SEM and HR-TEM. In the present study, we discuss the mechanism of formation of these self-assembled nanostructures, the morphology of the soft material and its thermal stability. We also demonstrate the utility of these soft materials in the field of plant tissue culture.

Introduction

β-*C*-Glycosides are becoming useful building blocks for the synthesis of 1-*O*-cinnamoylglucose derivatives, which can act as potential β-*C*-glycosidase inhibitors and have been reported to possess plant growth inhibitory activity.[1] In general, stereoselective synthesis of *C*-glycosides has attracted considerable interest, and the methodology has advanced significantly in the past decade.[2] Though some routes are available to synthesise β-*C*-glycosides, in practice their use is very limited due to their low yields, poor selectivity, or lack of general applicability leading to complicated procedures involved in synthetic steps. Typically, β-*C*-glycosides can be synthesised by addition of a nucleophilic reagent to a sugar lactone, giving the corresponding hemiacetal or exoglycal, which is then reduced by various reagents[3] or by Wittig or Grignard reaction at the anomeric position.[1d,2c,2p,4] α,β-Unsaturated-β-*C*-glycosidic ketones of D-glucose have served as the core moiety in natural ligands for making covalent bonds with many receptors, such as the peroxisome proliferator-activated receptor γ (PPARγ).[5] Moreover, β-*C*-glycosides can also act as non-hydrolyzable mimics of *N*- and *O*-glycosides and are useful in designing new chemotherapeutics and biological tools.[6] Saccharides and their derivatives have a wide range of applications[6,7] in the fields of materials, biology, drug design and natural product chemistry. In recent years, low molecular weight organogelators have played an important role in materials chemistry.[8] In particular, certain 4,6-*O*-protected-D-glucoses and D-mannoses possessing strong H-bond forming segments are prone to form gels even at low concentration.[9]

Molecular self-assembly is becoming a popular tool to construct different types of micro- and nanostructured materials.[10] Low molecular weight organogelators are known to self-assemble into various types of fibrils, strands, and tapes in organic solvents *via* weak intermolecular interactions.[11] In an organogel medium, one dimensional (1-D) supramolecular fibers are bundled up together and entangled at nodes, the so-called "junction point", to form three-dimensional (3-D) networks, in which the solvent molecules are trapped. The nanostructured functional molecular assembly thus created is a promising candidate for organic devices with intriguing photo- and electrochemical functions.[12] In the present study, we have synthesised and characterised a series of α,β-unsaturated-β-*C*-glycosidic ketones and found these derivatives to be excellent candidates for forming gels.

Plant tissue culture is the aseptic culture of cells, tissues, organs and their components under defined physical and chemical conditions *in vitro*. It is an important tool in both basic and applied studies, as well as in commercial applications,[13] and agar is currently commonly used.[14] Our studies aim to develop our new gelators as a substitute for agar, and with this in mind, we tested *Tribulus terrestris*, an annual plant of the Zygophyllaceae,[15] for plant tissue culture studies.

Experimental

Materials and methods

D-Glucose and various aromatic aldehydes used for the synthesis of soft materials were obtained from Sigma-Aldrich Chemicals Pvt. Ltd, USA, and were of high purity. The organocatalyst (pyrrolidine) was obtained from SRL, India. Other reagents, hydrochloric acid, sodium bicarbonate and solvents (AR Grade) were obtained in high purity from Sd-fine, India, and were used without any further purification. Column chromatography was performed on Silica Gel (100–200 mesh). NMR spectra were

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recorded on a Bruker DRX 300 MHz instrument, and differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 instrument. Scanning electron microscopy (SEM) images were recorded using a Hitachi-S-3400W microscope, and high-resolution transmission electron microscopy (HRTEM) was carried out on a JEOL JEM 3010 model (LaB_6 filament). Mass spectra were recorded using a Thermo Finnigan-ESI mass spectrometer, and optical rotation was performed using a Rudolph-Autopol II digital polarimeter. Elemental analyses were carried out on a Thermoquest microanalyser.

(4,6-*O*-Butylidene-β-D-glucopyranosyl)propan-2-one (2)

To a solution of 4,6-*O*-butylidene-D-glucopyranose (**1**) 2.34 g (10 mmol) in H_2O-THF (1 : 9) were added $NaHCO_3$ (4 equiv.) and 2,4-pentanedione (2 equiv.). The reaction mixture was stirred at reflux temperature for 36 h, then cooled to room temperature, allowed to stand for 2 h and the solution was filtered to remove the suspended $NaHCO_3$, followed by washing the residue well with DCM. Evaporation of the solvents followed by column chromatography purification (4 : 6 hexane–ethyl acetate) resulted in colourless solid. mp 102–104 °C; Yield: 2.32 g (85%) R_f 0.64 (0.5 : 9.5 hexane–ethyl acetate) **^{1}H NMR** (300 MHz, TMS, ppm): 4.44–4.47 (t, $J = 5.1$ Hz, 1H), 4.03–4.08 (m, $J = 9.9$ Hz, $J = 4.2$ Hz, 1H), 3.72–3.79 (m, 1H), 3.58–3.64 (t, $J = 8.7$ Hz, 1H), 3.11–3.38 (m, 4H), 2.96–2.99 (m, 2H), 2.79–2.86 (dd, $J = 3.9$ Hz, $J = 16.5$ Hz, 1H), 2.54–2.62 (q, $J = 8.0$ Hz, 1H), 2.13 (s, 3H), 1.52–1.59 (m, 2H), 1.31–1.39 (m, 2H), 0.83–0.88 (t, $J = 7.5$ Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 207, 102, 80, 76, 75, 74, 70, 68, 46, 36, 31, 17, 14; Elemental Anal. Found: C, 56.63; H, 8.26. Calc. for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08%

General procedure for (*E*)-1-(4,6-*O*-butylidene-β-D-glucopyranosyl)-4-phenylbut-3-en-2-one (4)

To a solution of β-*C*-glycosidic ketone, **2** (1 mmol) in dry DCM were added pyrrolidine (30% mol) and substituted benzaldehyde (**3a–q**) (1.2 mmol). After stirring at room temperature for given period of time, the reaction mixture was evaporated under reduced pressure and extracted with EtOAc–water. The ethyl acetate layer was dried over anhyd. Na_2SO_4 and concentrated to dryness. The product was further purified by flash column chromatography.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(phenyl)but-3-en-2-one 4a. Compound **4a** was obtained by the reaction of β-*C*-glycosidic ketone (**2**) (1 mmol, 0.274 g) and benzaldehyde (**3a**) (1.2 mmol, 0.12 ml) as a colorless solid: mp 192–194 °C; Yield: 0.31 g (86%); R_f 0.74 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 7.55–7.59 (m, 3H, Ar–H), 7.45–7.49 (m, 3H, Ar–H), 6.78 (d, $J = 16.8$ Hz, 1H), 4.79 (d, $J = 10.2$ Hz, 1H), 4.55 (t, $J = 4.7$ Hz, 1H), 4.06–4.11 (dd, $J = 3.6$ Hz, $J = 3.9$ Hz, $J = 10.1$ Hz, 1H), 3.87–3.94 (m, 1H), 3.61–3.68 (m, 1H), 3.13–3.44 (m, 5H), 2.81–2.89 (m, 1H), 1.65–1.68 (m, 2H), 1.55–1.60 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 198, 143, 134, 131, 129, 128, 126, 102, 81, 77, 75 (2C), 71, 68, 43, 36, 17, 14. Elemental Anal. Found: C, 66.38; H, 7.12. Calc. for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(2-hydroxyphenyl)but-3-en-2-one 4b. Compound **4b** was obtained by the reaction of β-*C*-glycosidic ketone (**2**) (1 mmol, 0.274 g) and 2-hydroxybenzaldehyde (**3b**) (1.2 mmol, 0.13 ml) as a colorless solid: mp 192–194 °C; Yield: 0.28 g (74%); R_f 0.74 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 7.82 (d, $J = 16.2$ Hz, 1H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.10–7.15 (t, $J = 7.8$ Hz, 1H), 6.86 (d, $J = 8.1$ Hz, 1H), 6.74–6.80 (m, 2H), 4.44–4.47 (t, $J = 4.8$ Hz, 1H), 3.97–4.01 (dd, $J = 3.6$ Hz, $J = 9.9$ Hz, 1H), 3.79–3.84 (t, $J = 8.7$ Hz, $J = 7.8$ Hz, 1H), 3.50–3.56 (t, $J = 8.4$ Hz, 1H), 3.29–3.35 (t, $J = 9.9$ Hz, 1H), 3.12–3.23 (m, 3H), 3.03–3.08 (m, 1H), 2.73–2.81 (dd, $J = 9.0$ Hz, $J = 7.2$ Hz, 1H), 1.52–1.58 (m, 2H), 1.31–1.41 (m, 2H), 0.81–0.86 (t, $J = 7.5$ Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 203, 162, 144, 136, 133, 131, 126, 124, 121, 107, 85, 81, 80 (2C), 75, 73, 48, 41, 22, 19; $[\alpha]_D^{30}$ −25.5 (*c* 1.0 in DMSO); Elemental Anal. Found: C, 63.41; H, 6.82. Calc. for $C_{20}H_{26}O_7$: C, 63.48; H, 6.93%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(2-hydroxy-3-methoxy-phenyl)but-3-en-2-one (4c). Compound **4c** was obtained by the reaction of β-*C*-glycosidic ketone (**2**) (1 mmol, 0.274 g) and *O*-vanillin (**3c**) (1.2 mmol, 0.182 g) as a colorless solid: mp 148–150 °C; Yield: 0.38 g (93%); R_f 0.8 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 7.85 (d, $J = 16.2$ Hz, 1H), 7.03 (d, $J = 7.5$ Hz, 1H), 6.72–6.83 (m, 3H), 4.44–4.47 (t, $J = 4.5$ Hz, 1H), 3.98–4.03 (dd, $J = 3.3$ Hz, $J = 6.3$ Hz, 1H), 3.82 (s, 3H), 3.53–3.59 (t, $J = 8.4$ Hz, 1H), 3.04–3.36 (m, 5H), 2.76–2.84 (q, $J = 8.4$ Hz, $J = 7.5$ Hz, 1H), 1.51–1.59 (m, 2H), 1.29–1.41 (m, 2H), 0.81–0.85 (t, $J = 7.5$ Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 199, 147, 146, 138, 127, 121, 120, 119, 112, 102, 81, 75(2C), 71, 68, 56, 43, 36, 17, 14; $[\alpha]_D^{30}$ −20.1 (*c* 1.0 in DMSO); Elemental Anal. Found: C, 62.02; H, 6.83. Calc. for $C_{21}H_{28}O_8$: C, 61.75; H, 6.91%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(2-hydroxy-5-bromophenyl)but-3-en-2-one (4d). Compound **4d** was obtained by the reaction of β-*C*-glycosidic ketone (**2**), (1 mmol, 0.274 g) and 5-bromo-2-hydroxybenzaldehyde (**3d**) (1.2 mmol, 0.241 g) as a colorless solid: mp 178–180 °C; Yield: 0.37 g (81%); R_f 0.83 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 7.71 (d, $J = 18.0$ Hz, 1H), 7.51 (d, $J = 7.8$ Hz, 1H), 7.17–7.20 (m, 1H), 6.72–6.81 (m, 2H), 4.44–4.46 (m, 1H), 3.97–4.00 (m, 2H), 3.02–3.79 (m, 6H), 2.71–2.79 (m, 1H), 1.52–1.54 (m, 2H), 1.31–1.36 (m, 2H), 0.81–0.83 (t, $J = 7.5$ Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 198, 156, 137, 134, 131, 127, 123, 118, 111, 102, 80, 76, 75, 74, 70, 68, 43, 36, 17, 14; Elemental Anal. Found: C, 52.18; H, 5.45. Calc. for $C_{20}H_{25}BrO_7$: C, 52.53; H, 5.51%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(3,4-dioxanephenyl)but-3-en-2-one (4e). Compound **4e** was obtained by the reaction of β-*C*-glycosidic ketone (**2**) (1 mmol, 0.274 g) and piperonal (**3e**) (1.2 mmol, 0.18 g) as a colorless solid: mp 199–201 °C; Yield: 0.35 g (86%); R_f 0.87 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 7.40 (dd, $J = 1.8$ Hz, $J = 16.2$ Hz, 1H), 6.97 (d, 2H), 6.73–6.76 (dd, $J = 1.8$ Hz, $J = 7.8$ Hz, 1H), 6.50–6.56 (dd, $J = 1.8$ Hz, $J = 15.9$ Hz, 1H), 5.95 (d, $J = 2.1$ Hz, 2H), 4.45–4.47 (m, 1H), 4.00–4.08 (m, 1H) 3.80–3.89 (m, 1H), 3.55–3.62 (m, 1H), 3.00–3.40 (m, 7H), 2.70–2.85 (m, 1H), 1.50–1.60 (m, 2H), 1.30–1.40 (m, 2H),

0.81–0.86 (m, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 198, 150, 148, 143, 129, 125 (2C), 109, 107, 102 (2C), 81, 77 (2C), 75 (2C), 71, 68, 43, 36, 17, 14; ESI-MS; Calc. for $C_{21}H_{26}O_8$ 406.16; *m*/*z* found, 407.13 (M + H$^+$); $[\alpha]_D^{30}$ −17.2 (*c* 0.16 in DMSO).

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(2-nitrophenyl)-but-3-en-2-one (4f). Compound **4f** was obtained by the reaction of β-*C*-glycosidic ketone (**2**) (1 mmol, 0.274g) and 2-nitro-benzaldehyde (**3f**) (1.2 mmol, 0.18 g) as a pale brown solid: mp 98–100 °C; Yield: 0.3 g (73%); R_f 0.83 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 7.91–8.00 (t, *J* = 13.5 Hz, 2H), 7.58 (s, 2H), 7.50 (d, *J* = 6.3 Hz, 1H), 6.55 (d, *J* = 16.2 Hz, 1H), 4.46 (s, 1H), 4.04–4.07 (t, 1H), 3.87 (s, 1H), 3.62–3.68 (t, *J* = 9.0 Hz, 1H), 3.09–3.39 (m, 5H), 2.86–2.93 (dd, *J* = 8.7 Hz, *J* = 7.2 Hz, 1H), 1.55 (d, *J* = 4.2 Hz, 2H), 1.31–1.38 (m, 2H), 0.82–0.87 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 198, 139, 134, 131 (2C), 130, 129, 125, 102, 80, 76, 75, 74, 71, 68, 43, 36, 17, 14; Elemental Anal. Found: C, 59.05; H, 6.26, N, 3.26. Calc. for $C_{20}H_{25}NO_8$: C, 58.96; H, 6.18; N, 3.44%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(5-thiophene-5′-thiophenyl)but-3-en-2-one (4g). Compound **4g** was obtained by the reaction of β-*C*-glycosidic ketone (**2**) (1 mmol, 0.274 g) and 2,2′-bithiophene-5-carbaldehyde (**3g**) (1.2 mmol, 0.23 g) as a pale brown solid: mp 156–160 °C; Yield: 0.34 g (76%); R_f 0.87 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 7.54 (d, *J* = 15.6 Hz, 1H), 7.26 (d, *J* = 4.8 Hz, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), 7.08 (d, *J* = 3.9 Hz, 1H), 6.96–6.99 (t, *J* = 4.2 Hz, 1H), 6.39–6.44 (d, *J* = 15.6 Hz, 1H), 4.42–4.45 (t, *J* = 5.7 Hz, 1H), 3.94–3.99 (dd, *J* = 3.9 Hz, *J* = 4.2 Hz, 1H), 3.73–3.81 (m, 2H), 3.46–3.52 (t, *J* = 8.7 Hz, 1H), 2.98–3.34 (m, 6H), 2.64–2.72 (dd, *J* = 9.0 Hz, *J* = 6.6 Hz, 1H), 1.49–1.55 (m, 2H), 1.30–1.40 (m, 2H), 0.79–0.84 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 196, 140, 138, 136, 135, 133, 128, 127, 126, 124 (3C), 101, 80, 78 (2C), 77, 74 (2C), 70, 68, 43, 36, 17, 14; Elemental Anal. Found: C, 58.48; H, 5.94. Calc. for $C_{22}H_{26}O_6S_2$: C, 58.64; H, 5.82%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(4′-phenyl)phenylbut-3-en-2-one (4h). Compound **4h** was obtained by the reaction of β-*C*-glycosidic ketone (**2**) (1 mmol, 0.274 g) and 4-biphenyl carboxaldehyde (**3h**) (1.2 mmol, 0.218 g) as a colorless solid: mp 200–202 °C; Yield: 0.4 g (92.6%); R_f 0.6 (9 : 1 chloroform–methanol); **^{1}H NMR** (300 MHz, TMS, ppm): 7.51–7.67 (m, 7H), 7.38–7.43 (t, *J* = 7.2 Hz, 2H), 7.29–7.34 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 16.2 Hz, 1H), 4.42–4.47 (t, *J* = 5.7 Hz, 1H), 3.92–3.97 (dd, *J* = 3.9 Hz, *J* = 4.2 Hz, 2H), 3.41–3.46 (t, *J* = 8.4 Hz, 1H), 3.27–3.33 (t, *J* = 9.6 Hz, 1H), 3.01–3.21 (m, 5H), 2.73–2.81 (dd, *J* = 6.9 Hz, *J* = 9 Hz, 1H), 1.48–1.52 (m, 2H), 1.31–1.38 (m, 2H), 0.82–0.87 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 197, 142 (2C), 139, 133, 126–128 (10C), 101, 81, 77, 74, 70, 68, 43, 36, 17, 14; ESI-MS: Calc. for $C_{26}H_{30}O_6$ 438.20, *m*/*z* found, 439.20 (M + H$^+$); $[\alpha]_D^{30}$ −87.6 (*c* 0.07 in DMSO).

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(5-bromo-3-pyridyl)but-3-en-2-one (4i). Compound **4i** was obtained by the reaction of β-*C*-glycosidic ketone (**2**) (1 mmol, 0.274 g) and 5-bromo-3-pyridine-carboxaldehyde (**3i**) (1.2 mmol, 0.223 g) as a colorless solid: mp 188–190 °C; Yield: 0.37 g (83.9%); R_f 0.43 (9 : 1 chloroform–methanol); **^{1}H NMR** (300 MHz, TMS, ppm): 8.68 (d, *J* = 35.1 Hz, 2H), 8.25 (s, 1H), 7.48 (d, *J* = 16.5 Hz, 1H), 6.97 (d, *J* = 16.2 Hz, 1H), 4.43–4.46 (t, *J* = 4.8 Hz, 1H), 3.90–3.95 (dd, *J* = 3.9 Hz, *J* = 4.5 Hz, 1H), 3.74–3.79 (t, *J* = 9.0 Hz, 1H), 3.00–3.58 (m, 8H), 2.70–2.79 (dd, *J* = 8.7 Hz, *J* = 7.2 Hz, 1H), 1.47–1.51 (m, 2H), 1.30–1.37 (m, 2H), 0.81–0.86 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 197, 151, 148, 137 (2C), 129, 101, 81, 76, 74 (2C), 70, 68, 44, 36, 17, 14; ESI-MS: Calc. for $C_{19}H_{24}BrNO_6$ 441.07, *m*/*z* found 444.07 (M + H$^+$); $[\alpha]_D^{30}$ −13.8 (*c* 1.0 in DMSO).

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(1,4-dioxane-phenyl)but-3-en-2-one (4j). Compound **4j** was obtained by the reaction of β-*C*-glycosidic ketone (**2**) (1 mmol, 0.274 g), 1,4-benzodioxan-6-carboxaldehyde (**3j**) (1.2 mmol, 0.197 g) as a colorless solid: mp 150–152 °C; Yield: 0.32 g (76%); R_f 0.87 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 7.40 (d, *J* = 16.5 Hz, 1H), 6.99 (d, *J* = 10.8 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 16.2 Hz, 1H), 4.44–4.47 (t, *J* = 5.1 Hz, 1H), 4.18–4.23 (m, 2H), 4.03–4.07 (dd, *J* = 3.9 Hz, *J* = 9.6 Hz, 1H), 3.80–3.87 (m, 1H), 3.62–3.68 (t, *J* = 3.3 Hz, 1H), 3.14–3.37 (m, 4H), 2.99–3.06 (dd, *J* = 3.6 Hz, *J* = 12.1 Hz, 1H), 2.84 (m, 3H), 1.52–1.59 (m, 2H), 1.28–1.41 (m, 2H), 0.82–0.85 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 198, 146, 143 (2C), 128, 125, 123, 118, 117, 102, 80, 77, 76, 75 (2C), 71, 68, 65, 64, 43, 36, 17, 14; Elemental Anal. Found: C, 63.04; H, 6.62. Calc. for $C_{22}H_{28}O_8$: C, 62.85; H, 6.71%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(4-nitrophenyl)-but-3-en-2-one (4k). Compound **4k** was obtained by the reaction of β-*C*-glycosidic ketone (**2**) (1 mmol, 0.274 g) and 4-nitro-benzaldehyde (**3k**) (1.2 mmol, 0.181 g) as a pale brown solid: mp 170–172 °C; Yield: 0.32 g (78.6%); R_f 0.85 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 8.15 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 16.2 Hz, 1H), 6.80 (d, *J* = 16.2 Hz, 1H), 4.22–4.45 (t, *J* = 4.8 Hz, 1H), 3.94–3.99 (m, 3H), 3.76–3.82 (m, 1H), 3.50–3.56 (t, *J* = 8.4 Hz, 1H), 3.27–3.33 (t, *J* = 10.8 Hz, 1H), 3.06–3.23 (m, 4H), 2.72–2.80 (dd, *J* = 8.7 Hz, *J* = 15.9 Hz, 1H), 1.45–1.52 (m, 2H), 1.26–1.36 (m, 2H), 0.78–0.83 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 197, 148, 139, 130, 128 (2C), 124 (2C), 102, 80, 77, 74, 70, 68, 43, 36, 17, 13; Elemental Anal. Found: C, 58.77; H, 5.98; N, 3.56. Calc. for $C_{20}H_{25}NO_8$: C, 58.96; H, 6.18; N, 3.44%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(9-anthranyl)-but-3-en-2-one (4l). Compound **4l** was obtained by the reaction of β-*C*-glycosidic ketone (**2**), (1 mmol, 0.274 g) and 9-anthral-dehyde (**3l**) (1.2 mmol, 0.247 g) as a yellow solid: mp 136–138 °C; Yield: 0.42 g (90.9%); R_f 0.83 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 8.40–8.47 (dd, *J* = 3.9 Hz, *J* = 17.7 Hz, 1H), 8.35 (d, *J* = 4.2 Hz, 1H), 8.09 (d, *J* = 4.5 Hz, 2H), 7.91 (d, *J* = 3.0 Hz, 2H), 7.40 (d, *J* = 4.2 Hz, 4H), 6.62–6.69 (dd, *J* = 4.2 Hz, *J* = 12.3 Hz, 1H), 4.47 (d, *J* = 3.9 Hz, 1H), 4.11–4.13 (t, *J* = 3.9 Hz, 1H), 4.05 (d, *J* = 7.5 Hz, 2H), 3.19–3.74 (m, 7H), 2.95–3.00 (t, *J* = 7.8 Hz, 1H), 1.55 (s, 2H), 1.34 (s, 2H), 0.83–0.86 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 198, 140, 135, 125–131 (14C), 102, 80, 77, 75 (2C), 71, 68, 43, 36, 17, 14; Elemental Anal. Found: C, 72.56; H, 6.31. Calc. for $C_{28}H_{30}O_6$: C, 72.71; H, 6.54%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(4,5-dimethoxyphenyl)but-3-en-2-one (4m). Compound **4m** was obtained by the reaction of β-*C*-glycosidic ketone (**2**), (1 mmol, 0.274 g) and 3,4-dimethoxybenzaldehyde (**3m**) (1.2 mmol, 0.199 g) as a colorless solid: mp 162–164 °C; Yield: 0.35 g (83%); R_f 0.76 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 7.25–7.30 (m, 1H), 6.86–6.92 (m, 1H), 6.67 (d, $J = 8.1$ Hz, 1H), 6.43 (d, $J = 15.9$ Hz, 1H), 4.3 (s, 1H), 3.81–3.86 (m, 2H), 3.7 (m, 6H), 3.37–3.42 (t, $J = 8.4$ Hz, 1H), 2.88–3.20 (m, 6H), 2.55–2.63 (m, 1H), 1.38 (d, $J = 6.8$ Hz, 2H), 1.18–1.22 (m, 2H), 0.65–0.69 (t, $J = 6.9$ Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 198, 149, 143, 127, 124, 123, 111, 110, 102, 86, 77, 75 (2C), 71, 68, 56 (2C), 43, 36, 17, 14; $[\alpha]_D^{30}$ −11.7 (*c* 1.0 in DMSO); Elemental Anal. Found: C, 62.72; H, 7.31. Calc. for $C_{22}H_{30}O_8$: C, 62.55; H, 7.16%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(ferrocyl)but-3-en-2-one (4n). Compound **4n** was obtained by the reaction of β-*C*-glycosidic ketone (**2**), (1 mmol, 0.274 g) and ferrocenecarboxaldehyde (**3n**) (1 mmol, 0.214 g) as a dark red solid was obtained with flash column chromatography. mp 150–152 °C; Yield: 0.38 g (81%) R_f 0.89 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 7.46 (d, $J = 13.8$ Hz, 1H), 6.32 (d, $J = 14.7$ Hz, 1H), 4.21–4.54 (m, 5H), 4.09 (m, 5H), 3.66–3.82 (m, 3H), 3.23–3.36 (m, 5H), 2.84–2.95 (m, 2H), 1.56 (s, 2H), 1.36 (s, 2H), 0.85 (s, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 198, 146, 124, 102, 81, 78, 75 (2C), 68–72 (12C), 43, 36, 17, 14; Elemental Anal. Found: C, 61.43; H, 6.23. Calc. for $C_{24}H_{30}FeO_6$: C, 61.29; H, 6.43%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(cinnamoyl)but-3-en-2-one (4o). Compound **4o** was obtained by the reaction of β-*C*-glycosidic ketone (**2**), (1 mmol, 0.274 g) and cinnamaldehyde (**3o**) (1.2 mmol, 0.15 ml) as a colorless solid: mp 208–210 °C; Yield: 0.24 g, (62%); R_f 0.70 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 7.43 (d, $J = 6.9$ Hz, 2H), 7.21–7.32 (m, 4H), 6.81–6.96 (m, 2H), 6.24 (d, $J = 15.3$ Hz, 1H), 4.20–4.45 (t, $J = 5.0$ Hz, 1H), 3.92–3.97 (m, 1H), 3.59–3.75 (m, 3H), 3.42–3.48 (t, $J = 8.4$ Hz, 1H), 3.26–3.32 (t, $J = 9.8$ Hz, 1H), 3.10–3.16 (m, 3H), 2.94–3.00 (m, 1H), 2.62–2.70 (dd, $J = 9.0$ Hz, $J = 15.9$ Hz, 1H), 1.47–1.54 (m, 2H), 1.29–1.37 (m, 2H), 0.80–0.85 (t, $J = 7.4$ Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 197, 142, 141, 136, 130, 129, 128, 127, 126, 102, 80, 76, 74 (2C), 70, 68, 43, 36, 17, 14; ESI-MS: Calc. for $C_{22}H_{28}O_6$, 388.19; *m*/*z* found, 389.40 ($M + H^+$); $[\alpha]_D^{30}$ −12.7 (*c* 1.0 in DMSO).

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(2-pyridyl)but-3-en-2-one (4p). Compound **4p** was obtained by the reaction of β-*C*-glycosidic ketone (**2**), (1 mmol, 0.274 g) and 2-pyridinecarboxaldehyde (**3p**) (1.2 mmol, 0.128 g) as a colorless solid: mp 138–140 °C; Yield: 0.19 g, (52%); R_f 0.61 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 8.61 (d, $J = 4.2$ Hz, 1H), 7.70–7.75 (t, $J = 7.2$ Hz, 1H), 7.45–7.55 (m, 2H), 7.25–7.29 (m, 1H), 7.14–7.20 (m, 1H), 4.43–4.47 (t, $J = 4.8$ Hz, 1H), 4.01–4.06 (dd, $J = 3.9$ Hz, $J = 9.6$ Hz, 1H), 3.84–3.91 (m, 1H), 3.63–3.69 (t, $J = 8.7$ Hz, 1H), 3.10–3.39 (m, 9H), 2.81–2.89 (m, 1H), 1.51–1.55 (m, 2H), 1.27–1.39 (m, 2H), 0.80–0.85 (t, $J = 7.4$ Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 198, 153, 150, 141, 138, 130, 125 (2C), 102, 81, 76, 75 (2C), 71, 68, 44, 36, 17, 14; $[\alpha]_D^{30}$ −9.0 (*c* 1.0 in DMSO); Elemental Anal. Found: C, 62.72; H, 6.74; N, 3.60. Calc. for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85%.

(*E*)-1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)-4-(3-pyridyl)but-3-en-2-one (4q). Compound **4q** was obtained by the reaction of β-*C*-glycosidic ketone (**2**), (1 mmol, 0.274 g) and 3-pyridinecarboxaldehyde (**3q**) (1.2 mmol, 0.128 g) as a colorless solid: mp 147–149 °C; Yield: 0.20 g, (55%); R_f 0.34 (0.5 : 9.5 hexane–ethyl acetate); **^{1}H NMR** (300 MHz, TMS, ppm): 8.70 (br, 1H), 8.55 (br, 1H), 7.33–7.93 (m, 3H), 6.79 (d, $J = 16.2$ Hz, 1H), 4.47 (d, $J = 4.8$ Hz, 1H), 3.99–4.09 (m, 1H), 3.79–3.85 (t, $J = 7.8$ Hz, 1H), 3.08–3.56 (m, 9H), 2.74–2.83 (m, 1H), 1.54 (d, $J = 4.5$ Hz, 2H), 1.31–1.38 (m, 2H), 0.80–0.85 (t, $J = 7.2$ Hz, 3H); **^{13}C NMR** (75 MHz, TMS, ppm): 197, 150, 149, 138, 134, 128, 102, 80, 76, 74 (2C), 70, 68, 43, 36, 17, 13; $[\alpha]_D^{30}$ −33.7 (*c* 1.0 in DMSO); Elemental Anal. Found: C, 63.11; H, 6.83; N, 3.76. Calc. for $C_{19}H_{25}NO_6$: C, 62.80; H, 6.93; N, 3.85%.

Gelation test

Gelation was tested for 8 solvents or mixtures of solvents. The gelation test was carried out as follows: the gelator was mixed in a capped test tube with appropriate amount of solvent, and the mixture was heated until the solid was dissolved. By this procedure the solvent boiling point becomes higher than that under standard atmospheric pressure. The sample vial was allowed to cool in air to 25 °C, left for 1 h at this temperature, and the tube was then turned upside-down. When the result at this stage was a clear or slightly opaque gel, it was denoted by "G".

Plant tissue culture method

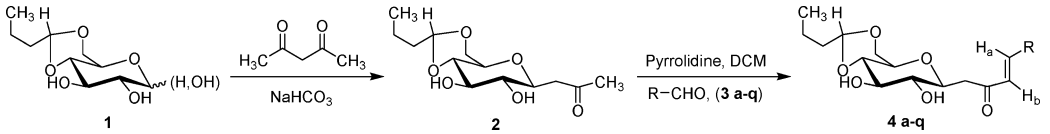
Leaves were collected from well-grown plants, and washed thoroughly under running tap water without damage to the tissues. The leaves were surface-sterilized with (1%) sodium hypochlorite for 20 min followed by (0.5%) mercuric chloride for 3 min and finally 3 to 5 times in sterilized distilled water under aseptic conditions. The leaves were cut into small pieces and inoculated into Murashige Skoog (MS) medium with different concentrations of α-naphthaleneacetic acid (NAA) with addition of 0.8% (w/v) agar and 3% (w/v) sucrose. The culture tubes were capped with cotton plugs and autoclaved at 121 °C for 15 min. The cultures were incubated under a 16 h light/8 h dark cycle, and were inspected regularly for the induction of callus. The callus, once formed on the MS medium (with agar), was sub-cultured on MS medium containing 0.75% **4i**, which was used instead of agar. All experiments were carried out in triplicate.

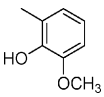
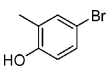
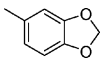
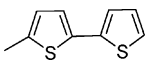
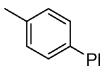
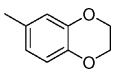
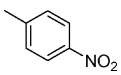
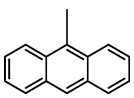
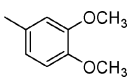
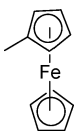
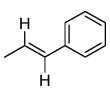
Results and discussion

1. Synthesis and characterization of α,β-unsaturated-β-*C*-glycosidic ketones

4,6-*O*-Butylidene-D-glucopyranose (**1**) was synthesized from D-glucose.[16] 1-(4,6-*O*-Butylidene-β-D-glucopyranosyl)propan-2-one (**2**) was synthesised from compound **1** in good yield by following a procedure similar to that in the literature.[17] Aldol condensation of β-*C*-glycoside **2** with various aromatic and heteroaromatic aldehydes (**3a–q**) was carried out at ambient temperature in the presence of a catalytic amount of pyrrolidine (30 mol%) (Table 1). To optimize the reaction conditions, condensation was carried out using three organic solvents

Table 1 Synthesis of α,β-unsaturated-β-*C*-glycosidic ketones **4a–q**.



	R	Time/h	Yield (%)	NMR data for products **4a–q**		
				$\delta(H_a)$/ppm	$\delta(H_b)$/ppm	$^3J(H_a,H_b)$/Hz [a]
a		4	86	6.78	—[b]	16.8, —[b]
b		6	74	6.77	7.82	—[b], 16.2
c		6	93	6.78	7.85	—[b], 16.2
d		8	81	6.77	7.71	—[b], 18.0
e		4	86	6.53	7.40	15.9, 16.2
f		12	73	6.55	7.96	16.2, —[b]
g		10	76	6.42	7.54	15.6, 15.6
h		5	93	6.79	7.51–7.67	16.2, —[b]
i		7	84	6.96	7.47	16.2, 16.5
j		5	76	6.55	7.40	16.2, 15.9
k		10	79	6.80	7.49	16.2, 16.2
l		15	91	6.65	8.43	12.3, 17.7
m		7	83	6.42	—[b]	15.9, —[b]
n		12	81	6.31	7.46	14.7, 13.8
o		8	62	6.23	—[b]	15.3, —[b]
p		8	52	—[b]	—[b]	—[b], —[b]
q		8	55	—[b]	6.79	—[b], 16.2

[a] Coupling constants as determined from the H_a and H_b peaks are given separately. [b] Peaks overlapped with aromatic protons.

(chloroform, DCM and CH_3CN) and also three different bases (pyrrolidine, NaOH and triethylamine). Moderate to good yields (70–90%) of α,β-unsaturated-β-*C*-glycosidic ketones (**4a–q**) was obtained by using DCM in the presence of pyrrolidine as an organocatalyst. ^{1}H NMR spectrum of the α,β-unsaturated-β-*C*-glycosides (**4a–q**) showed a signal around 6.5–7.0 ppm for H_a (nearest the aromatic moiety) and 7.3–7.8 ppm for H_b (nearest the carbonyl group) (Table 1). A similar observation has been reported for "*E*"-isomeric phenylpropenoid-β-D-glucopyranoside [7.83 (d, J = 15.6 Hz), 6.57 (dt, J = 15.6, J = 5.6 Hz)].[18] Moreover, the coupling constant ($^3J_{Ha,Hb}$) observed shows the existence of the "*E*"-isomer (Table 1). Furthermore, the presence of unsaturated carbonyl group is confirmed from the ^{13}C NMR spectrum [δ(C=O) ~197 ppm]. In these α,β-unsaturated-β-*C*-glycosidic ketones (**4a–q**), a signal at around 6.5–8.0 ppm corresponds to the aromatic protons and those for the protecting group were observed around 2.5–4.0 ppm.

2. Single-crystal XRD studies

In general, gelator molecules tend to pile up in a one-dimensional direction, resulting in needle-like crystals or an amorphous solid, and this makes it difficult to obtain a single crystal suitable for XRD studies from organogelators, **2**, **4e**, **4i** and **4p**. However, we were able to obtain single crystals suitable for XRD analysis from the compounds **4b** and **4q**. In the absence of XRD data for **4e**, **4i** and **4p**, characterization of **4b** and **4q** helps us to understand the self-assembly, hydrogen bonding and π–π stacking in organic solvents.

ORTEP views of compounds **4b** and **4q** are shown in Fig. 1 and 2 respectively. In molecule **4b**, strong hydrogen bonding interactions O(1)–H(1)···O(2), O(3)–H(3A)···O(1) and O(4)–H(4A)···O5 result in the formation of chains of molecules with overlapping phenyl moieties, as shown in Fig 3. The existence of a β-anomeric form and an "*E*"-isomeric form of **4b** and **4q** is identified from the corresponding torsion angles [**4b**: H(11)–C(11)–C(12)–H(12) = 177.86° and C(1)–C(7)–C(8)–C(9) = 179.3(2)°] and [**4q**: H(1)–C(1)–C(2)–H(2) = 179.08° and C(12)–C(13)–C(14)–C(15) = 178.53(18)°]. In the case of **4q**, there are strong H-bonding interactions between the free hydroxyl group (C(2)–OH) and the pyridyl nitrogen (N) [C(2)–O(5)···N = (2.917(3) Å] and the free hydroxyl group (C(3)–OH) and the carbonyl (C=O) [C(3)–O(4)···O(6) = (2.917(2) Å)]. The hydrogen bonding and π–π stacking arrangement of **4q** is shown in Fig. 4. Crystallographic data for both **4b** and **4q** are given in Table 2.

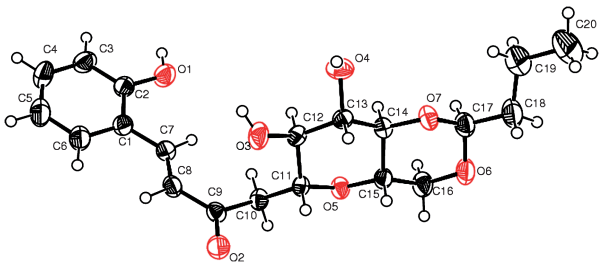


Fig. 1 ORTEP view of **4b**.

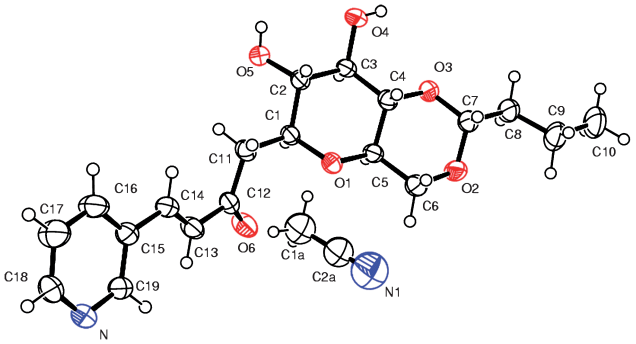


Fig. 2 ORTEP view of **4q**.

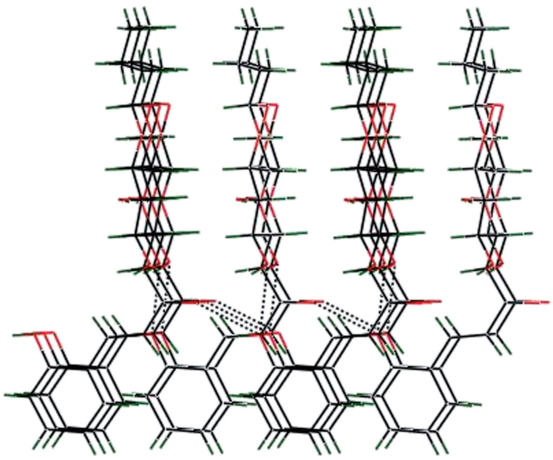


Fig. 3 H-bonding interactions and π–π stacking of **4b**.

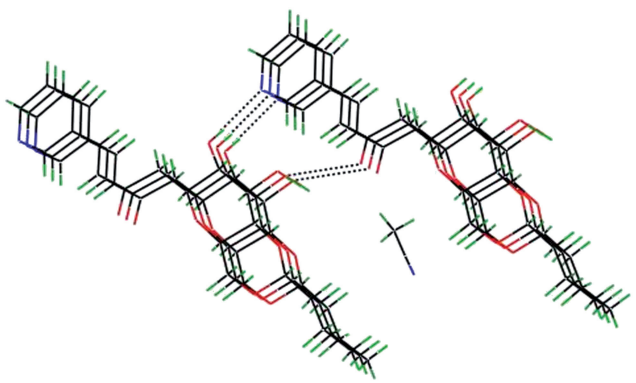


Fig. 4 H-bonding interactions and π–π stacking of **4q**.

3. Gelation studies

From the test tube inversion method, we conclude that compounds **4e**, **4i** and **4p**, which bear the partially protected sugar moiety, gelate three, four and two solvent molecules respectively, of the eight solvents tried (Table 3). However, β-*C*-glycoside **2**, the precursor of **4a–q**, also forms a gel. Of the different derivatives, **4i** (bearing the pyridyl group with a 5-bromo substituent) is an excellent gelator [critical gelation concentration (CGC): **4e** (1.2%), **4i** (0.75%) and **4q** (1.0%)]. Compound **4i** is insoluble in water, but when it is solubilized

Table 2 Crystallographic data for compounds **4b** and **4q**.

Parameters	**4b**	**4q**
Formula	$C_{20}H_{26}O_7$	$C_{21}H_{28}N_2O_6$
Formula weight	378.41	404.45
Crystal system	Monoclinic	Triclinic
Space group	$P2_1$	$P1$
a (Å)	4.9409(7)	4.8023(2)
b (Å)	33.746(5)	9.3324(3)
c (Å)	5.7154(9)	12.6403(4)
α (deg)	90	70.868(2)
β (deg)	101.967(9)	80.910(2)
γ (deg)	90	77.056(2)
V (Å^3)	932.2(2)	519.41(3)
Z	1	2
Calculated density (Mg/m^3)	1.348	1.293
μ (mm^{-1})	0.102	0.095
T (K)	293(2)	293(2)
No. of unique reflections	2268	4287
No. of observed reflections	9350	11660
$R1$, Rw	0.0376, 0.0962	0.0430, 0.1160
GOF	1.080	1.098
Crystal habit	Colorless prisms	Colorless needles

Table 3 Solvents tested for gelation with **3**, **4e**, **4i** and **4p**.[a]

Solvent	**2**	**4e**	**4i**	**4p**
Water	S	I	I	S
Methanol	G	G	G	G
Ethanol	G	G	G	G
DMSO + H_2O	S	S	G	S
DMF + H_2O	S	S	G	S
Acetonitrile	S	G	P	S
Dichloroethane	G	S	I	P
Chloroform	G	I	I	S

[a] G, S, P and I denote gelation, solvation, precipitation and insoluble respectively.

using the minimum amount of DMF/DMSO, further addition of H_2O leads to the formation of a gel.

4. Structural relationship

Of the 17 α,β-unsaturated-β-*C*-glycosidic ketones tested, **4e**, **4i** and **4p** form a gel. In order to understand why this is, the role of the substituents on the aromatic moiety was examined. Compound **4e** (possessing 1,3-dioxane) was found to be a gelator, whereas the presence of additional methylene group in the dioxane (1,4-dioxane, **4j**) was not. In addition to this, compounds **4i** and **4p** (possessing 5-bromo-3-pyridyl and 2-pyridyl groups, respectively) were gelators, **4i** being better than **4p**. These observations show that the presence of bromine in these heterocyclic derivatives plays a vital role in gelation. However, gelation was not observed with the 3-pyridyl derivative (**4q**). Thus, even a small modification of molecule leads to a drastic change in the gelation properties. From these results, we believe that in addition to the hydrogen bonding and π-stacking, weak interactions play a vital role.

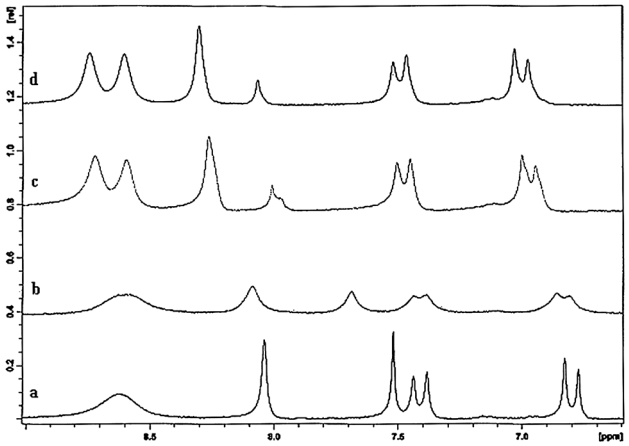


Fig. 5 ^{1}H NMR spectra (aromatic region) of **5i** recorded using different ratios of $CDCl_3$–DMSO-d_6: (a) 4 : 1; (b) 3 : 2; (c) 2 : 3; (d) 1 : 4.

5. NMR studies of gelator 4i

Of the β-*C*-glycosidic ketones, only **4i** shows broad peaks in the aromatic region, which may be due to the organogelating nature of this compound influencing the broadening of the aromatic protons. Broadening of NMR signals can be induced by various processes, such as aggregation and ligand exchange. However, definitive interpretation for such behavior requires careful analysis. In our case, further evidence for the positive influence of the association of molecules was obtained from the ^{1}H NMR studies of **4i** using different ratios of solvent in the mixture (Fig. 5).

From the 2D NMR studies (Fig. 6), the appearance of cross-peaks at 8.3, 8.6 and 8.75 ppm in 1 : 4 $CDCl_3$–DMSO-d_6 (Fig. 6a) indicates the coupling of H_a, H_b and H_c respectively, attributed to the absence of aggregation. However, in 4 : 1 $CDCl_3$–DMSO-d_6 Fig. 6b), the cross-peaks are absent, due to molecular aggregation which results in the upfield shift of H_a. These results show that the pyridyl moiety is engaged with molecular aggregation in the gelation process.

6. Microscopy studies

The self-assembled aggregates of gelators, **2**, **4e** and **4i** were studied by SEM (Fig. 7). Two types of aggregation mode were observed: fibrous and lamellar.

Compounds **4e**, **4i** and **4p** exhibit a fibrous aggregated morphology, whereas the corresponding β-*C*-glycoside precursor **2** has a lamellar structure. Fibrous structures can incorporate more solvent than the lamellar structures because of their greater void volumes (300–500 nm in diameter) as is shown by SEM and HRTEM. This seems to explain why **4e**, **4i** and **4p** are better organogelators than the precursor **2**; indeed, similar observations were reported with a sugar-appended azonaphthol gelator.[19] In the SEM image of gelator **2**, the larger flat tubules are composed of fibrous network as shown in Fig. 7a. The bulk structure of this organogelator **2** is lamellar, and the high-magnification image shows a dense fibrous network (Fig 7a,b). Compounds **4e**, **4i** and **4p** did not show a lamellar structure, but they did have three-dimensional fibrous networks with a breadth of less than 100 nm (Fig. 8).

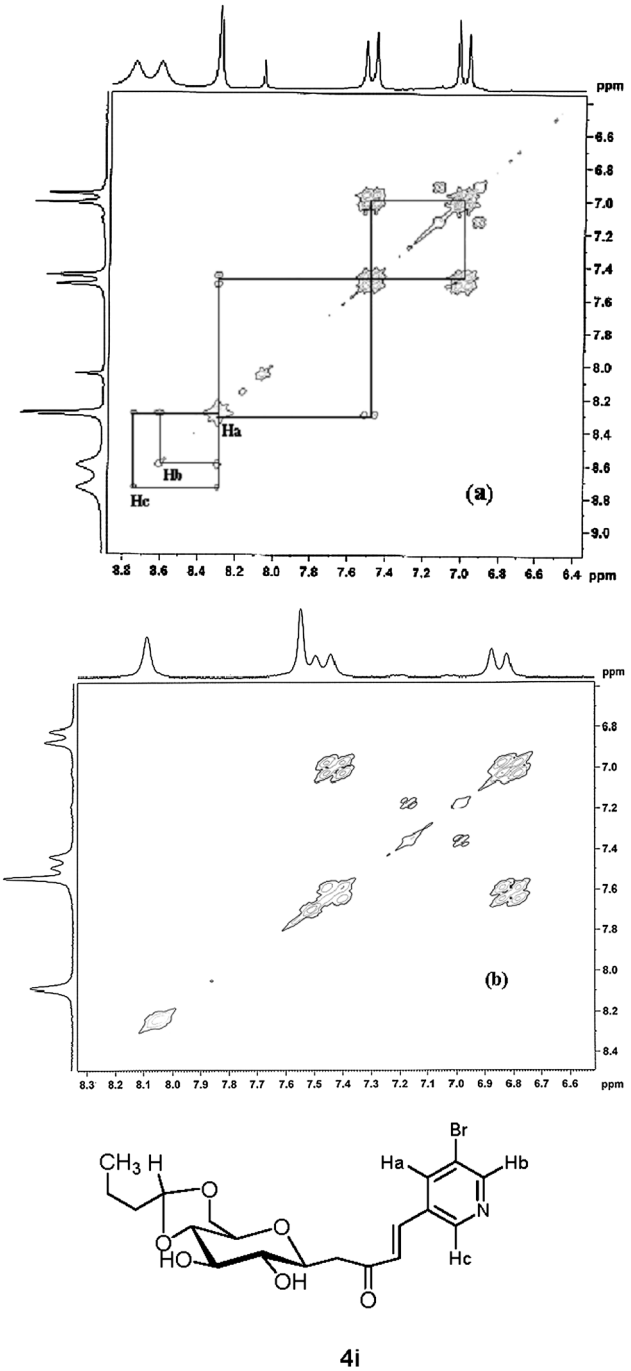


Fig. 6 ^{1}H–^{1}H COSY spectrum (aromatic region) of **4i** recorded using different ratios of $CDCl_3$–DMSO-d_6: (a) 1 : 4; (b) 4 : 1.

7. Thermal studies

To study the thermal properties of the organogelators **4e** and **4i**, we obtained data from DSC (Fig. 9). The melting peak of **4e** is 199.4 °C in the solid phase with $\Delta H = 95.12$ J/g, and 197.4 °C in the gel phase with $\Delta H = 9.67$ J/g. In comparison, the melting peak of **4i** is 186.8 °C in the solid phase with $\Delta H = 13.94$ J/g, and 92.5 °C in the gel phase with $\Delta H = 284.3$ J/g. In general, the ΔH value for the gel is dependent on the nature of the solvent (molecular weight, hydrophilicity and density) – a similar type of observation has been reported in the literature.[20]

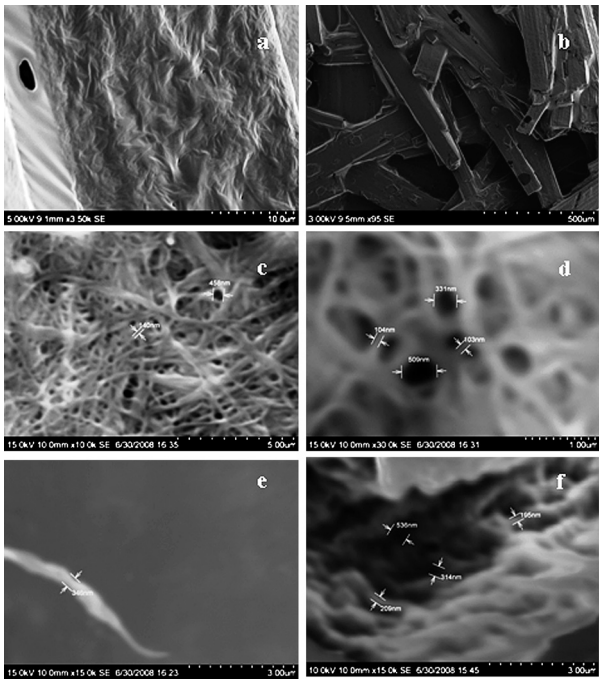


Fig. 7 SEM images (with different magnification) of: **2** in $CHCl_3$ [(a) 10 μm; (b) 500 μm]; **4i** in MeOH [(c) 5 μm; (d) 1 μm]; and **4e** in MeOH [(e) 3 μm; (f) 3 μm].

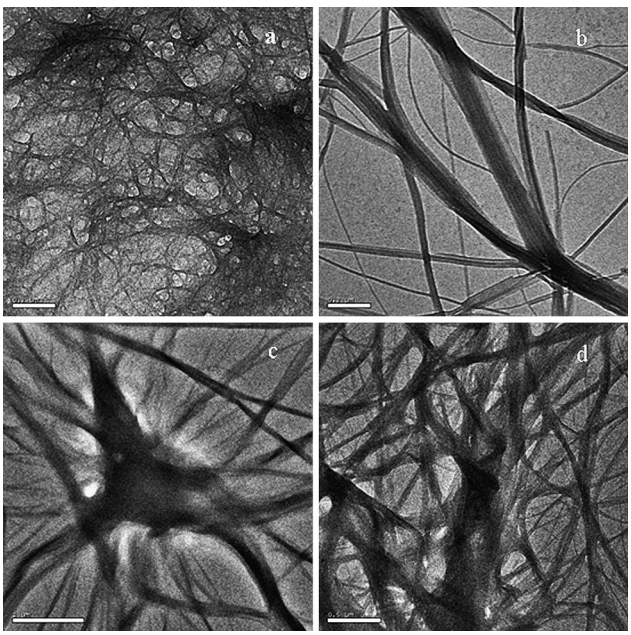


Fig. 8 HRTEM images of: (a) **4e** in EtOH; (b) **4i** in DMSO–H_2O; (c) **4p** in EtOH (1 μm); (d) **4p** in EtOH (500 nm).

The peak at 77.6 °C in the case of **4e** and **4i** in gel phase is due to the liberation of solvent (*i.e.*, ethanol). The peaks observed at 93.9 °C in solid phase and at 74.3 °C in gel phase of **4i** are due to liberation of water (moisture) and solvent (ethanol) respectively. The boiling point (transition temperature) of ethanol is 78.5 °C, whereas the transition temperature of

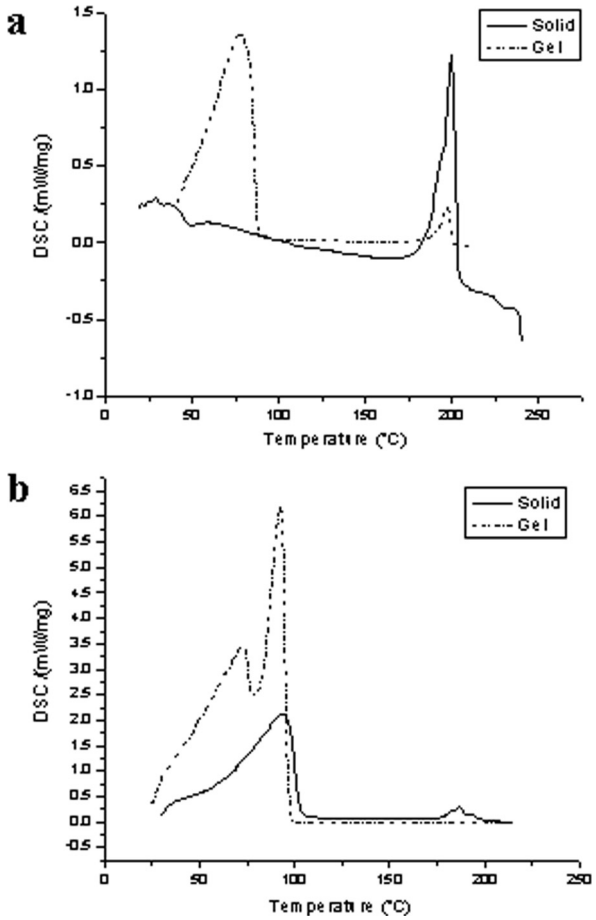


Fig. 9 Differential scanning calorimetry (DSC) of (a) **4e** and (b) **4i**.

the solvent present in the gelator is lower, due to a gelator–solvent interaction rather than a solvent–solvent interaction. Thus our study indicates that organogelators **4e** and **4i** have good thermal stability and can form solid-like gels in organic solvents.

8. Demonstration as a soft material for plant tissue culture

En masse, undifferentiated parenchymatous cells are known as a callus. Their induction from leaf explants was observed on MS medium with 0.8% agar and different concentrations of NAA (0.2–0.5 mg/L). Callus initiation was observed from the 9th day onwards, and maximum callus was obtained on MS medium supplemented with 0.5 mg/L of NAA. Subculture was performed on the 28th day after initial culture, with the medium having the same composition as MS medium except for the absence of agar (Fig. 10). The subculture was split into two groups; first group used sterilized medium and second used unsterilized medium. It is interesting to note that neither sterilized nor unsterilized media were contaminated by microorganisms, indicating that **4i** has antimicrobial activity. The gelator used in the media did not harm the growth of the callus. From these results, we conclude that (*E*)-1-(4,6-*O*-butylidene-β-D-glucopyranosyl)-4-(5-bromo-3-pyridyl)but-3-en-2-one (**4i**) can be used as a antimicrobial gel for solidifying media.

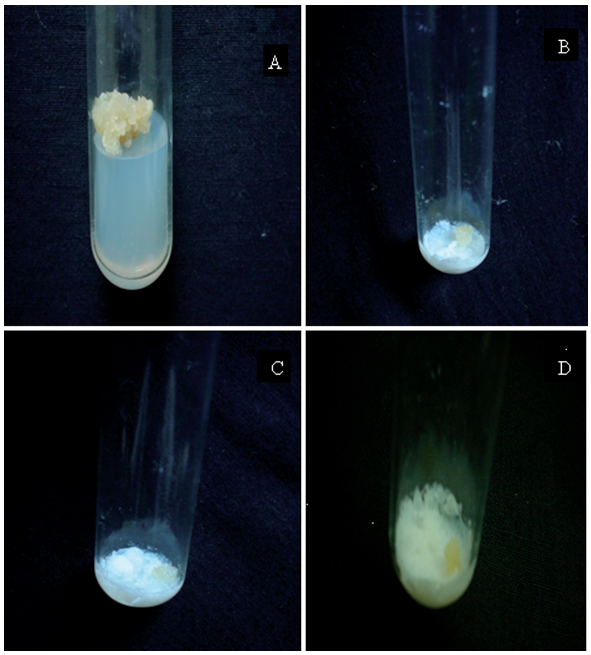


Fig. 10 Callus formation observed from leaf explants: (A) MS medium with agar; (B) sterilized MS medium with **4i**; (C) unsterilized MS medium with **4i**; (D) sterilized MS medium with **4i** (34th day).

Conclusions

A series of D-glucose-based soft materials were obtained in the form of self-assembled nanofibers using facile synthetic procedures, and characterised by 1D and 2D NMR experiments. Even small modifications of the molecules led to the drastic changes in the gelation properties. Gels result even at low concentrations (critical gelation concentration 0.75%), and structural characterization clearly shows the presence of a three-dimensional fibrous network. DSC studies of these soft materials show that they are thermally stable. Of the various gelators synthesised, (*E*)-1-(4,6-*O*-butylidene-β-D-glucopyranosyl)-4-(5-bromo-3-pyridyl)but-3-en-2-one (**4i**) was found to be an ideal alternative gelling agent for plant tissue culture. Further studies in this area are in progress.

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