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Aryl 4,6-*O*-arylidene-1-thio-β-D-glycopyranoside-based new organogelators and their gels

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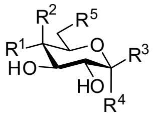
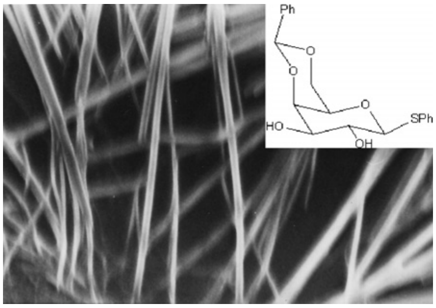
ABSTRACT

Aryl 4,6-*O*-arylidene-1-thio-β-D-glycopyranosides based on glucose and galactose form organogels in benzene, toluene, *o*- and *p*-xylene and 1,2,3,4-tetrahydronaphthalene. The gel morphologies of micro and nano dimensions were studied using SEM and TEM. Absorption spectroscopic studies of two organogels in benzene revealed that CH–π or π-stacking along with intermolecular H-bonding is responsible for the gel assembly.



R^2,R^4 = H; R^1,R^5 = $OCHC_6H_5$; R^3 = SPh
R^1,R^4 = H; R^2,R^5 = $OCHC_6H_5$; R^3 = SPh
R^2,R^4 = H; R^1,R^5 = OCH-*p*-$NO_2C_6H_4$; R^3 = SPh
R^1,R^4 = H; R^2,R^5 = OCH-*p*-$NO_2C_6H_4$; R^3 = SPh
R^2,R^4 = H; R^1,R^5 = OCH-*p*-$NO_2C_6H_4$; R^3 = STol
R^1,R^4 = H; R^2,R^5 = OCH-*p*-$NO_2C_6H_4$; R^3 = STol



1. Introduction

Because of potential applications for light-harvesting materials,[1a,b] solar cells,[1c] semiconductors,[1d] magneto-optical switches,[1e] sensorics,[1f] transcription of organic templates,[1g–i] crystal engineering,[1j] etc., studies of organogels[2] have been of increasing interest during the last two decades. Organogels are formed by entrapment and immobilization of liquids into the three-dimensional network formed from self-assembling molecules during gelation from a solution of the organogelator. Intermolecular forces responsible for such gel assembly are H-bonding, π-stacking, and London dispersion forces among others.[3]

Among the growing list of organogelators and their corresponding gels,[4] reports of sugar-based organogels have gained considerable interest.[5] The main advantage of dealing with carbohydrates is that, by exploiting the basic skeleton of different diastereomers in a sugar family, it is possible to systematically design various aggregates. During preparation of thioglycoside-derived glycosyl donors for synthesis of oligosaccharides, we observed the gelation of benzene and toluene by phenyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**7a**). Based on our preliminary observations and also on the fact that we were inspired by Shinkai's work on analogous organogels derived from corresponding methyl glycosides,[5d,h–k,m] we have prepared other aryl 4,6-*O*-arylidene thioglycosides (Scheme 1) and report herein, their synthesis along with the morphological and spectroscopic studies of some representative organogels.

2. Results and discussion

Phenyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**7a**) and phenyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (**7b**) were synthesized, respectively, from D-glucose and D-galactose following the literature procedure.[6] Other thioglycosides (**5a–5b** and **6a–6b**) were also similarly converted to the corresponding phenyl- and thiotolyl 4,6-*O*-*p*-methoxybenzylidene-1-thio-β-D-gluco- (**9a** and **12a**) and galactopyranosides (**9b** and **12b**). For the preparation of analogous *p*-nitrobenzylidene compounds (**8a**, **8b**, **11a**, and **11b**), phenyl and tolylthio glycopyranosides (**5a**, **5b**, **6a**, and **6b**) were

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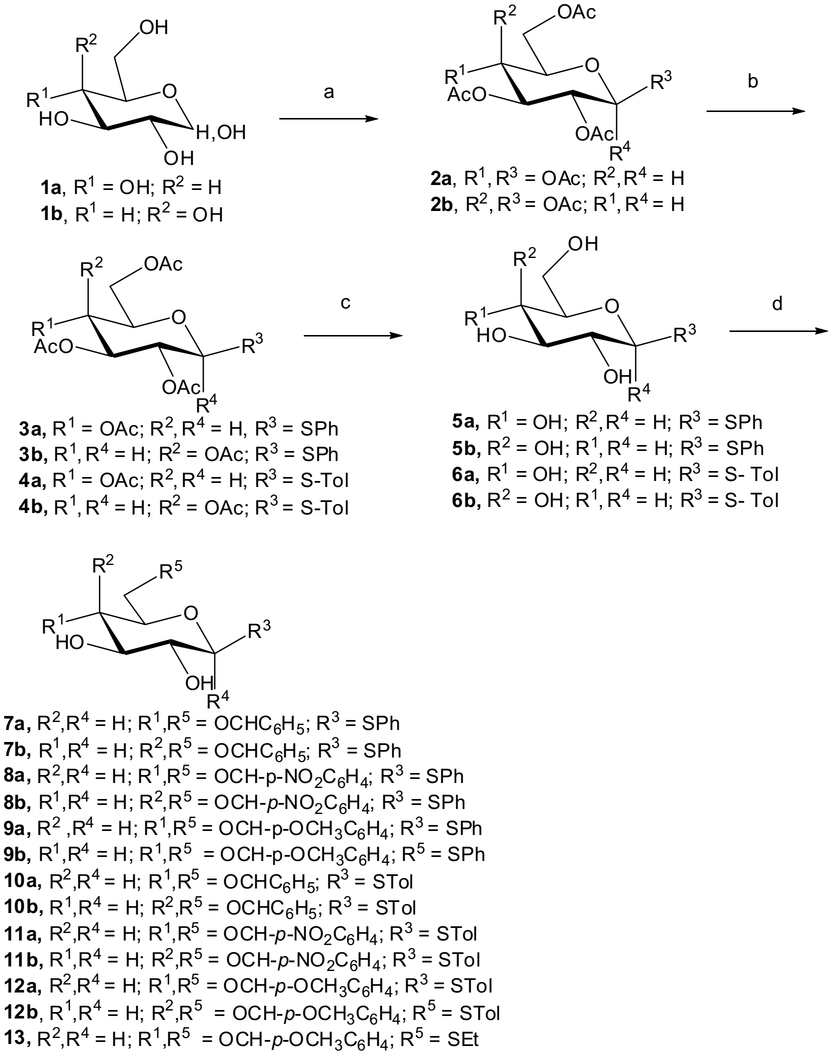

1a, R^1 = OH; R^2 = H
1b, R^1 = H; R^2 = OH

2a, R^1,R^3 = OAc; R^2,R^4 = H
2b, R^2,R^3 = OAc; R^1,R^4 = H

3a, R^1 = OAc; R^2,R^4 = H, R^3 = SPh
3b, R^1,R^4 = H; R^2 = OAc; R^3 = SPh
4a, R^1 = OAc; R^2,R^4 = H; R^3 = S-Tol
4b, R^1,R^4 = H; R^2 = OAc; R^3 = S-Tol

5a, R^1 = OH; R^2,R^4 = H; R^3 = SPh
5b, R^2 = OH; R^1,R^4 = H; R^3 = SPh
6a, R^1 = OH; R^2,R^4 = H; R^3 = S- Tol
6b, R^2 = OH; R^1,R^4 = H; R^3 = S- Tol

7a, R^2,R^4 = H; R^1,R^5 = $OCHC_6H_5$; R^3 = SPh
7b, R^1,R^4 = H; R^2,R^5 = $OCHC_6H_5$; R^3 = SPh
8a, R^2,R^4 = H; R^1,R^5 = OCH-p-$NO_2C_6H_4$; R^3 = SPh
8b, R^1,R^4 = H; R^2,R^5 = OCH-*p*-$NO_2C_6H_4$; R^3 = SPh
9a, R^2 ,R^4 = H; R^1,R^5 = OCH-p-$OCH_3C_6H_4$; R^3 = SPh
9b, R^1,R^4 = H; R^1,R^5 = OCH-p-$OCH_3C_6H_4$; R^5 = SPh
10a, R^2,R^4 = H; R^1,R^5 = $OCHC_6H_5$; R^3 = STol
10b, R^1,R^4 = H; R^2,R^5 = $OCHC_6H_5$; R^3 = STol
11a, R^2,R^4 = H; R^1,R^5 = OCH-*p*-$NO_2C_6H_4$; R^3 = STol
11b, R^1,R^4 = H; R^2,R^5 = OCH-*p*-$NO_2C_6H_4$; R^3 = STol
12a, R^2,R^4 = H; R^1,R^5 = OCH-*p*-$OCH_3C_6H_4$; R^3 = STol
12b, R^1,R^4 = H; R^2,R^5 = OCH-*p*-$OCH_3C_6H_4$; R^5 = STol
13, R^2,R^4 = H; R^1,R^5 = OCH-*p*-$OCH_3C_6H_4$; R^5 = SEt

Scheme 1. Synthesis of aryl 4,6-*O*-arylidene-1-thio-β-D-glycopyranosides. Reagents and conditions: (a) fused NaOAc, Ac_2O; (b) RSH, $BF_3·Et_2O$, dry CH_2Cl_2 (R = SPh/*p*-Stol); (c) NaOMe, dry MeOH; (d) (dimethoxymethyl)benzene, *p*TSA (cat), dry DMF, toluene, 55 °C, diminished pressure/1-(dimethoxymethyl)-4-methoxybenzene, *p*TSA (cat), dry DMF, toluene, 55 °C, diminished pressure/1-(dimethoxymethyl)-4-nitrobenzene, *p*TSA (cat), dry DMF, toluene, 110 °C, Dean–Stark apparatus.

refluxed separately with *p*-nitrobenzaldehyde in the presence of a catalytic amount of *p*-toluenesulfonic acid in 9:1 DMF–toluene with simultaneous removal of water. The results of the syntheses of **7a**–**13** are shown in Table 1. All of these compounds (**7a**–**13**) were examined with different liquids to check their sol–gel properties. Of these compounds **7a**, **7b**, **8a**, **8b**, **11a**, and **11b** gelatinized benzene, toluene, xylene (*o*- and *p*-), and 1,2,3,4-tetrahydronaphthalene (Table 2). Representative examples have been chosen for morphological and spectroscopic studies of the corresponding organogels.

Table 1
Synthesis of aryl 4,6-*O*-arylidene-1-thio-β-D-glycopyranosides

Compounds	Typical method[a]	Time (h)	Yield (%)/mp
7a	A	20–22	90/178 °C/(174 °C)[7]
7b	A	20–22	85/119 °C/(118 °C)[7]
8a	B	35–36	79/170 °C
8b	B	27	70/182 °C
9a	A	35–36	85/168 °C/(168 °C)[8]
9b	A	27	73/156 °C/(157 °C)[9]
10a	A	.45	85/173 °C/(171–172 °C)[10]
10b	A	20–22	70/154 °C/(154–155 °C)[11]
11a	B	35–36	75/194 °C
11b	B	35–36	70/183 °C
12a	A	35–36	83/175 °C/(176–178 °C)[12]
12b	A	35–36	68/156 °C/(156–158 °C)[12]
13	A	18–20	88/146 °C[13]

[a] For methods A and B see Section 3. Data within parentheses represent corresponding literature values.

The morphology of the gel can be obtained by scanning electron microscopy (SEM) or by transmission electron microscopy (TEM). An SEM image of the xerogel from 0.55 wt % of **7a** in benzene exhibited sponge-like structure (Fig. 1a), whereas that in toluene showed a three-dimensional network (Fig. 1b). The SEM of **7b** in benzene displayed a fibrous network (Fig. 1c), and the TEM of **8b** in benzene showed thread-like structures (Fig. 1d) with nano dimensions (average diameter 11.2 nm).

The concentration dependence of T_{gel} of gelators **7a** and **7b** in benzene, respectively, (Fig. 2a and b) indicates the stability of these gels with concentration.

The FTIR spectra of **7a** and **7b** at different concentrations in benzene in the sol and gel phases are shown in Figure 3a and b, respectively. A strong peak appears at 3582 cm^{-1} at the lower concentration (5.09×10^{-3} M) of **7a** in benzene (Fig. 3a). The intensity of the peak at 3582 cm^{-1} increases at higher concentration (1.52×10^{-2} M) in the sol state, but at this concentration in the

Table 2
Gelation test of organogelators in various liquids[a]

Entry	Organic solvent	7a	7b	8a	8b	11a	11b
1	Benzene	G	G	G	G	G	G
2	Toluene	G	G	G	G	G	G
3	*o*-Xylene	G	G	OG	OG	OG	OG
4	*p*-Xylene	G	G	OG	OG	OG	OG
5	1,2,3,4-Tetrahydronaphthalene	G	G	OG	OG	OG	OG
6	Pyridine	S	S	S	S	S	S
7	Dichloromethane	S	S	S	S	S	S
8	Chloroform	S	S	S	S	S	S
9	Methanol	P	P	P	P	P	P
10	Ethanol	P	P	P	P	P	P
11	2-Propanol	P	P	P	P	P	P
12	Butanol	P	P	P	P	P	P
13	Cyclohexanol	P	P	P	P	P	P
14	Diethyl ether	I	I	I	I	I	I
15	Diphenyl ether	P	P	P	P	P	P
16	Acetone	S	S	S	S	S	S
17	Cyclohexanone	S	S	S	S	S	S
18	Petroleum ether	I	I	I	I	I	I
19	Hexane	I	I	I	I	I	I
20	Cyclohexane	I	I	I	I	I	I

[a] G, gel; OG, opaque gel; S, solution; P, precipitate; I, insoluble.

gel state, the peak intensity at 3582 cm^{-1} is reduced with simultaneous appearance of a broad intense peak (3504–3167 cm^{-1}) centered at 3385 cm^{-1}, indicating the presence of an HO$\cdots$H bonded structure in the gel state.

In the case of the galactose-derived related organogelator (**7b**) at low concentration (5.09×10^{-3} M) in benzene solution, the peak appearing at 3686 cm^{-1} (strong) also appears in benzene solution at a higher concentration (1.52×10^{-2} M) with lowering of the intensity of this peak, which again vanishes at this concentration in the gel state (Fig. 3b). Sharp peaks at 3574 and 3576 cm^{-1} at low concentration (5.09×10^{-3} M) and in sol state at gel concentration (1.52×10^{-2} M) in benzene, change to a broad intense band (3645–3107 cm^{-1} centering at 3420 cm^{-1}) in its gel state. The shifts of stretching frequencies for sol and gel states in both of the cases of **7a** and **7b** indicate involvement of intermolecular H-bonding during gel assembly.

UV spectroscopy provides important information regarding the type of aggregation in a gel.[4j,14] UV spectra of **7a** and **7b** in benzene (Fig. 4a and b) at different concentrations (5.09×10^{-3} M and 1.52×10^{-2} M) in sol and in gel states indicate red shifts of absorption peak in case of the gelator **7a** in the gel state compared to those in the corresponding sol states. The red shift on increasing the gelator concentration indicates possibility of J-type aggregation of gelators starting even before gelation. The primarily associated gelators in the sol further aggregate in the gel state, and at this stage intermolecular H-bonding plays an important role as also evidenced from the corresponding IR spectra (Fig. 4a). It may be mentioned here that analogous ethyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**13**) did not gelate in benzene or toluene, and compounds (**9a**, **9b**, **12a**, and **12b**) having a *p*-substituent on the benzylidene aromatic ring with a +R effect (for example, OMe) are not organogelators. Thus, CH–π or π-stacking intermolecular forces might be playing some role in the aggregation of **7a**, and probably the benzylidene aromatic ring acts as an acceptor and the aglycon aromatic ring plays the donor role during stacking. Almost no change in the peak positions (λ_{max} 273.6 nm), as well as in the intensity of the UV spectra, of gelator **7b** at its gel concentration in both the sol and gel states (Fig. 4b) indicates involvement of mutually operative J- and H-type aggregations (ultimately exhibiting no change in peak positions) during gelation.

The combined UV and IR spectra of gelators **7a** and **7b** thus indicate that the initial aggregation of gelators probably starts through stacking (π– or CH–π-forming threads), which further assemble via intermolecular H-bonding and finally form a gel.

Important information regarding gel aggregation may be provided by ^{1}H NMR spectroscopy of gelators in both the sol and gel phases.[4g,5d] With this end in view, and also to understand the gelation process further, we recorded the ^{1}H NMR spectra (Fig. 5a and b) of the gelators **7a** and **7b** in the sol (at different concentrations in benzene-d$_6$) and gel phases at both ambient and elevated temperatures (beyond the mp of the gel at 60 °C).

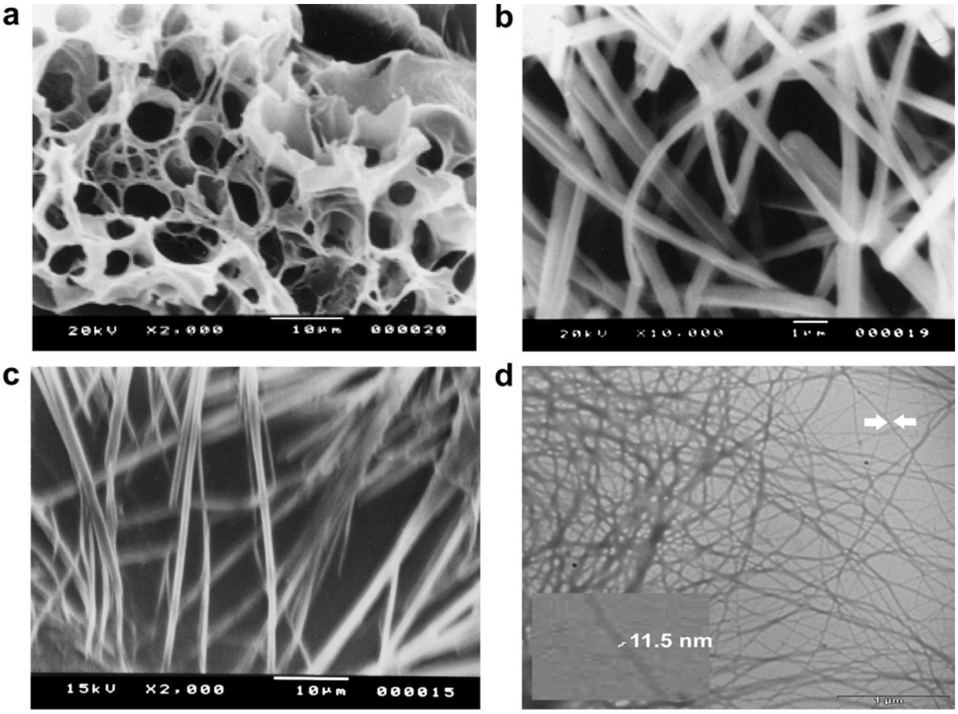

Figure 1. (a) and (b): SEM images of xerogels of **7a** in benzene and in toluene respectively; (c) SEM images of the xerogel of **7b** in toluene; (d) TEM image of **8b** in toluene.

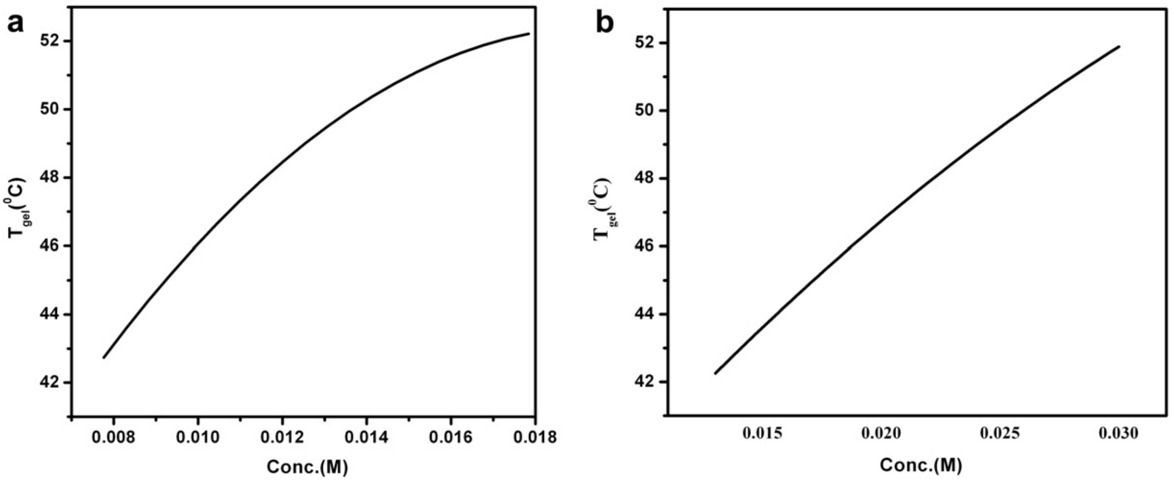

Figure 2. Concentration dependence of T_{gel} of gelators (a) **7a** in benzene and (b) **7b** in benzene.

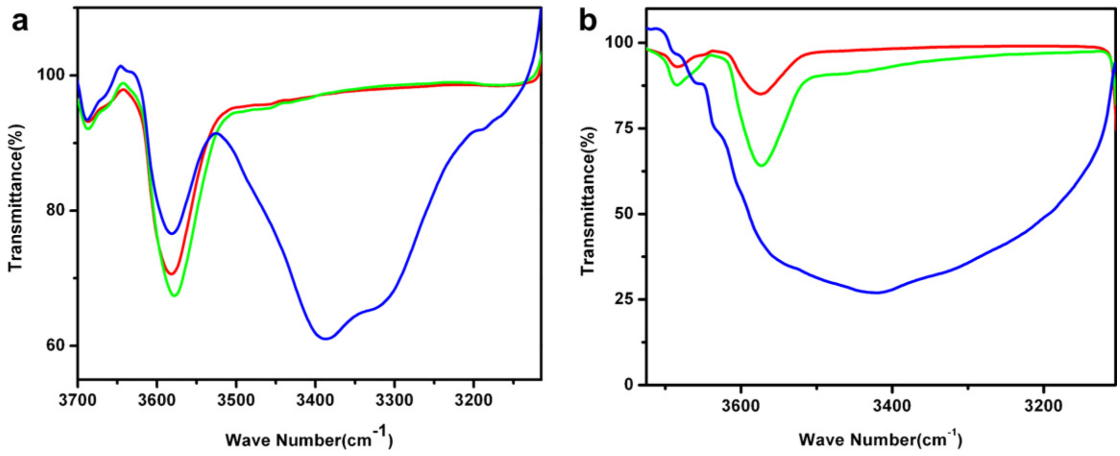

Figure 3. FTIR spectra at different concentrations (a) of gelator **7a** and (b) of gelator **7b** in benzene: 🟥 5.09×10^{-3} M solution; 🟩 1.52×10^{-2} M sol; 🟦 1.52×10^{-2} M gel.

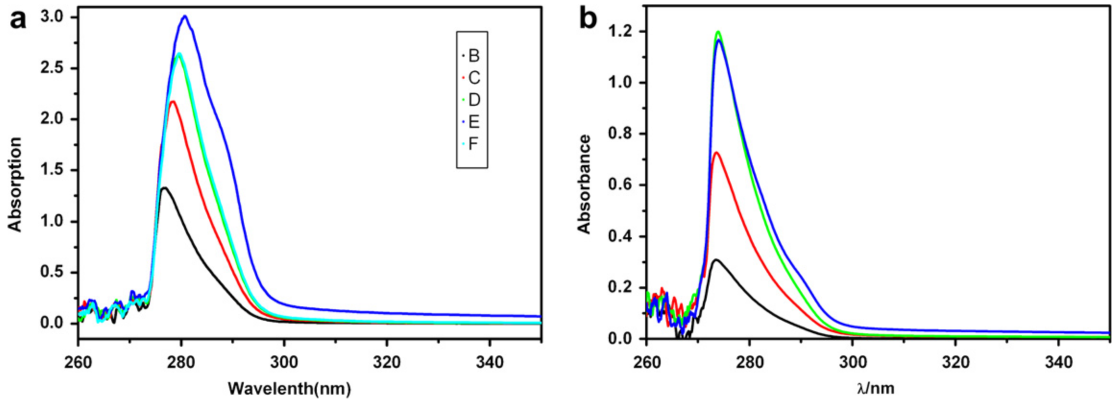

Figure 4. UV spectra at different concentrations (a) of gelator **7a** and (b) of gelator **7b** in benzene: ⬛ 5.09×10^{-3} M solution; 🟥 1.01×10^{-2} M solution; 🟦 1.52×10^{-2} M solution; 🟦 1.52×10^{-2} M gel; 🟩 1.52×10^{-2} M molten gel.

An increase in the concentration of the gelator **7a** from 5.09×10^{-3} M to 1.01×10^{-2} M shifts the hydroxy protons (appearing as a broad singlet) downfield (spectra IV and V shown in Fig. 5a). That this shift is not due to H-bonding is evidenced from the corresponding IR spectra of **7a** at these two concentrations (Fig. 3a). The shift is probably due to some deshielding anisotropy arising out of the initiation of the aggregation of gelator molecules below their gel concentrations. The two hydroxy peaks are, however, shifted upfield, still appearing as a broad singlet at gel concentration (1.52×10^{-2} M) in the gel state, in spite of intermolecular

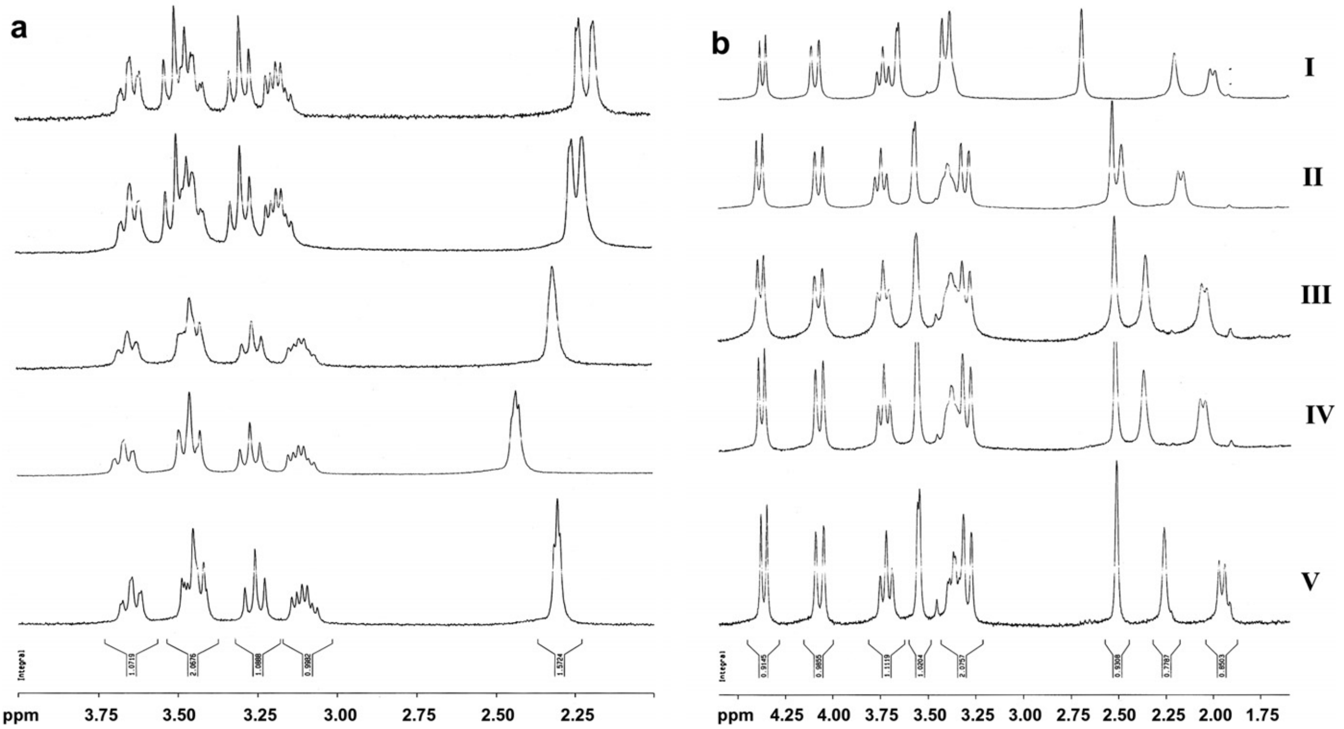

Figure 5. ^{1}H NMR spectra (a) of gelator **7a** and (b) of gelator **7b** at various concentrations in benzene-d_6: **I**: 1.52×10^{-2} M sol at 60 °C; **II**: 1.52×10^{-2} M sol at 25 °C; **III**: 1.52×10^{-2} M gel at 25 °C; **IV**: 1.01×10^{-2} M sol at 25 °C; **V**: 5.09×10^{-3} M sol at 25 °C.

H-bonding being operative at this stage (Fig. 3a). Thus the upfield shifting might be appearing due to some shielding anisotropy resulting from the three-dimensional gel assembly. The splitting of the hydroxy protons and further upfield shifting of the peak positions at gel concentration in the molten (sol) state could be due to the combined effects of the breaking of the H-bonding and of some network structure. An increase of the concentration of gelator **7b** (from 5.09×10^{-3} M to 1.01×10^{-2} M) changes the hydroxy peak positions downfield (spectra IV and V shown in Fig. 5b), which is not due to H-bonding as evidenced from the corresponding IR spectra (Fig. 3b). The shift may be caused by deshielding anisotropy out of initiation of some aggregation of the gelators at this stage. No further shift in hydroxy peak positions (see spectrum III of Fig. 5b) at the gel concentration (1.52×10^{-2} M) in the gel state might be due to the counterbalancing of both the deshielding and shielding anisotropies from intermolecular H-bonding and gel assembly, respectively, at this stage. Downfield shifting of hydroxy proton peaks in the molten gel state (at room temperature) is, however, not clear.

3. Experimental

3.1. Materials and methods

1,1-Dimethoxytoluene and 1,1′-dimethoxy-4-methoxytoluene were purchased from Alfa Aesar. All other reagents and solvents were purchased from SRL, India. Column chromatography was done on silica gel (60–120 mesh). All solvents were dried and/or distilled (as required) before use. Melting points were determined using a Toshniwal melting apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 341 LC Polarimeter. FTIR spectra were recorded on Perkin–Elmer RX-1 spectrometer. UV spectra were taken using a Shimadzu UV 1601 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer operating at 300 MHz and 75 MHz for the ^{1}H and ^{13}C modes, respectively. Mass spectrometric data were acquired by the electrospray-ionization method using a Q-TOF-Micro quadruple mass spectrophotometer. In all cases where the spectra of gels were recorded, the gel was formed by cooling the corresponding sol at gel concentration in the UV or IR cells or in the NMR tube. SEM pictures of the xerogels were taken using a JEOL ISN 5200 scanning microscope. All the TEM images were obtained using a TECHNAI G^{2+} transmission electron microscope.

Compounds **7a**,[7] **7b**,[7] **9a**,[8] **9b**,[9] **10a**,[10] **10b**,[11] **12a**,[12] **12b**[12] and **13**[13] were prepared according to known literature methods (Method A).[6] All compounds gave ^{1}H NMR spectra and melting points that correlated with those reported. New compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy and HRMS.

3.2. Experimental procedures for the preparation of 4,6-*O*-arylidene acetals

3.2.1. Method A

5a or **5b** or **6a** or **6b** was dissolved in minimum volume of dry DMF along with 15 mol % of pTSA and 1.5 equiv of benzaldehyde dimethoxy acetal. Dry toluene was added, and the mixture was kept under diminished pressure at 60 °C with stirring for several hours.

3.2.2. Method B

0.367 mmol of **8a** or **8b** or **11a** or **11b** was dissolved in a minimum volume of dry DMF along with 15 mol % (9.5 mg) of *p*TSA and 1.1 equiv (70 mg) of *p*-nitrobenzaldehyde. Dry toluene (9 times of DMF) was added, and the mixture was refluxed for several hours (Table 1) in Dean–Stark apparatus with simultaneous removal of water.

After completion of the reactions (following Method A or B), the solvents were evaporated under reduced pressure, and the resulting residue was dissolved in EtOAc (10 mL). The extract was washed with satd $NaHCO_3$, followed by water. The organic layer was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was crystallized from MeOH.

3.3. Representative data of compounds

3.3.1. Compound 8a

117 mg, 79%; mp 170 °C; $[\alpha]_D^{25}$ −59.0 (*c* 1, $CHCl_3$); UV: λ_{max}^{abs} 255 nm in $CHCl_3$. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.67 (s, 1H), 2.79 (s, 1H), 3.45–3.51 (t, 1H, *J* = 9.8 Hz), 3.53–3.61 (m, 2H), 3.78–3.91 (m, 2H), 4.39–4.4 (m, 1H), 4.63–4.67 (d, 1H, *J* = 9.8 Hz), 5.62 (s, 1H), 7.30–7.37 (m, 3H), 7.53–7.56 (m, 2H), 7.66–7.59 (d, 2H, *J* = 8.5 Hz), 8.21–8.24 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 68.59, 70.32, 72.85, 74.47, 80.22, 88.74, 100.14, 123.48, 127.48, 128.54, 129.19, 131.29, 132.98, 143.25, 148.37; HRMS: $[M+Na]^+$ calcd: 428.0780; found 428.0787.

3.3.2. Compound 8b

104 mg, 70%; mp 182 °C; $[\alpha]_D^{25}$ −31.0 (*c* 1, $CHCl_3$); UV: λ_{max}^{abs} 255.2 nm in $CHCl_3$. ^1H NMR ($CDCl_3$, 300 MHz): δ *2.52–2.58* (m, 2H), 3.60 (s, 1H), 3.65–3.74 (m, 2H), 4.05–4.09 (d, 1H, *J* = 12.6 Hz), 4.27–4.28 (d, 1H, *J* = 8.8 Hz), 4.39–4.43 (d, 1H, *J* = 11.9 Hz), 4.51–4.54 (d, 1H, *J* = 8.8 Hz), 5.61 (s, 1H), 7.26–7.38 (m, 3H), 7.55–7.58 (d, 2H, *J* = 8.4 Hz), 7.65–7.68 (d, 2H, *J* = 7.2 Hz), 8.20–8.23 (d, 2H, *J* = 8.76 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 68.64, 69.26, 69.76, 73.56, 75.41, 87.07, 99.59. 113.33, 127.55, 128.28, 128.84, 130.54, 133.71, 143.77, 148.33; HRMS: $[M+Na]^+$ calcd: 428.0780; found 428.0785.

3.3.3. Compound 11a

110 mg, 75%; mp 194 °C; $[\alpha]_D^{25}$ −48.0 (*c* 1, $CHCl_3$); UV: λ_{max}^{abs} 264.4 nm in $CHCl_3$. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.36 (s, 3H), 2.71 (s, 1H), 2.84 (s, 1H), 3.39–3.57 (m, 3H) 3.76–3.89 (m, 2H), 4.37–4.42 (dd, 1H, *J* = 10.6 and 4.3 Hz), 4.55–4.59 (d, 1H, *J* = 9.7 Hz), 5.59 (s, 1H), 7.14–7.17 (d, 2H, *J* = 7.9 Hz), 7.42–7.44 (d, 2H, *J* = 8.1 Hz), 7.65–7.68 (d, 2H, *J* = 8.7 Hz), 8.19–8.22 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.18, 68.61, 70.33, 72.70, 74.42, 80.25, 88.88, 100.13, 123.48, 127.17, 127.48, 129.95, 133.65, 138.99, 143.27, 148.37; HRMS: $[M+Na]^+$ calcd: 442.0936; found 442.0933.

3.3.4. Compound 11b

102 mg, 70%; mp 183 °C; $[\alpha]_D^{25}$ −37 (*c* 1, $CHCl_3$). UV: λ_{max}^{abs} 265.01 nm in $CHCl_3$. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.35 (s, 3H), 2.50–2.54 (m, 2H), 3.55 (s, 1H), 3.67–3.70 (m, 2H), 4.0–4.04 (d, 1H, *J* = 12.4 Hz), 4.20 (s, 1H), 4.35–4.39 (d, 1H, *J* = 12.4 Hz), 4.49–4.52 (d, 1H, *J* = 8.1 Hz), 5.47 (s, 1H), 7.12–7.15 (d, 2H, *J* = 7.9 Hz), 7.40–7.43 (d, 2H, *J* = 8.0 Hz), 7.64–7.66 (d, 2H, *J* = 8.7 Hz), 8.17–8.20 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.18, 68.64, 69.26, 69.76, 73.56, 75.41, 87.07, 99.59, 123.48, 127.17, 127.48, 129.95, 133.65, 138.99, 143.27, 148.37; HRMS: $[M+Na]^+$ calcd: 442.0936; found 442.0931.

3.4. General procedure for the T_{gel} experiment

A measured quantity of gelator was taken in a sealed-cap vial and a measured volume of gelation solvent was added. The vial was corked and heated in a water bath so that the gelator dissolved in the solvent. The solution was then cooled in an ice bath until the gel formed. The vial was then heated slowly in a water bath until the gel completely melted. The temperature at which the gel completely melted was recorded as T_{gel} (Fig. 2a and b).

4. Conclusion

Thus, among the 4,6-*O*-arylidene-1-thio-β-D-glycopyranosides, those containing a phenyl or a *p*-tolyl group on the anomeric sulfur atom and a phenyl or a *p*-nitrophenyl group on the arylidene moiety can gelate benzene, toluene, *o*- and *p*-xylenes, and 1,2,3,4-tetrahydronaphthalene. Spectroscopic studies reveal that CH–π or π-stacking and H-bonding are responsible for the supramolecular gel assembly. Further work is ongoing to utilize these thioglycosides for the synthesis of homooligo- or homopolysaccharides via regio- and stereoselective glycosidation in the gel state.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.06.005.

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