‘Bifunctional’ sugar-integrated gelators for organic solvents and water—on the role of nitro-substituents in 1-*O*-methyl-4,6-*O*-(nitrobenzylidene)-monosaccharides for the improvement of gelation ability

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The influence of modifications at the benzylidene protection group on the gelation ability of 1-*O*-methyl-4,6-*O*-benzylidene-monosaccharides was investigated. For α-D-glucose and α-D-mannose the ability for self-aggregation was found to be significantly extended by the introduction of a *p*-nitro-substituent. As a result, a new type of the so called ‘bifunctional gelators’, that are able to gelate to the same extent nonpolar and aromatic solvents as well as alcohols and water, was obtained. This effect was found to be strictly limited to nitro-substituents in the *para*-position. In contrast, *ortho*- and *meta*-derivatives show a drastic decrease in the gelation ability for all types of solvents. CD spectroscopy and experiments with solvent mixtures suggest that two aggregation modes are used for different solvents. In nonpolar liquids the establishment of hydrogen-bonds rules the self-aggregation process, whereas in protic solvents such as alcohols and water other aggregation modes such as hydrophobic interactions and dipole–dipole interactions are likely to be the main driving forces for gelation. To characterise the morphology of the gel network scanning electron microscopy (SEM) was carried out with the xerogels. Thus, this paper describes a new and facile method to design robust and versatile low molecular weight gelators.

Introduction

Motivated by the numerous applications for gels, formed by dilute solutions of polymers, proteins and inorganic substances,[1] development of new low molecular weight gelators for organic solvents and the investigation of their particular self-assembly properties have recently received much attention. They not only gelate various organic solvents but also create novel networks with fibrous superstructures, that can be characterised by scanning electron microscopy (SEM) pictures of xerogels.[2–13] The self-assembly of these gelling agents with fiber-like structures, that entangle to form a three dimensional (3D) network, is able to prevent the solvent from flowing, similar to their macromolecular and inorganic counterparts.[14] Gelators have been classified according to their driving forces for molecular aggregation into two categories: non-hydrogen-bond-based gelators and hydrogen-bond-based gelators. Cholesterol derivatives[7–10] are typical examples of the former group whereas aliphatic amide and urea derivatives[2–5] and saccharide-containing gelators[9,15–17] are the main representatives of the latter group.

In particular, saccharide-containing gelators are advantageous because of their facile molecular design using the rich carbohydrate library. 1-*O*-Methyl-4,6-*O*-benzylidene derivatives of monosaccharides have been intensively investigated in regard to their applicability as low molecular weight gelators. They stabilise organogels through establishment of rigid, strong and highly directional hydrogen-bonds proved by NMR spectroscopy and FTIR investigations of the gels in organic solvents.[17b] The absolute configuration of the monomer correlates significantly with the ability to gelate solvents. The optimal requirements for these compounds to be classified as a gelator are fulfilled only by derivatives of D-mannose and D-galactose.[17b,e] 1-*O*-Methyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**1**) occupies an intermediate position as a moderate gelator between gelating and non-gelating compounds.[17e] In general, for this class of compounds the analysis of the molecular arrangement in a single crystal was found to be a valuable strategy for the prediction of their gelation ability.[17d,f] After exhaustive elucidation of the relation between the hydrogen-bonding array in the sugar moiety and their gelation behaviour we turned our attention to the influence of the benzylidene protection group on the self-aggregation phenomenon. A challenging goal is the design of robust gelators which are applicable to protic solvents (particularly water) where the hydrogen-bonding interaction cannot be used as a driving force for molecular assembly. A possible approach to the problem consists of the enhancement of non-hydrogen-bonding interactions, such as hydrophobic interactions, dipole–dipole interactions *etc*. In this paper we report that the presence of a nitro-substituent in the 4,6-*O*-benzylidation group results in a remarkable change in the gelation spectrum. Some methyl 4,6-*O*-(*p*-nitrobenzylidene) derivatives exhibit, in contrast to their non-nitro derivatives, a gelation ability for nonpolar aromatic solvents *and* polar solvents like alcohols. Surprisingly, even water is gelated by these gelators. CD-spectroscopy and gelation experiments with solvent mixtures lead to the assumption that different aggregation types are true for different types of solvents, suggesting the polymorphological nature of these gelators. In nonpolar solvents the aggregation of monomers is driven by a hydrogen-bonding interaction, whereas in polar solvents hydrophobic interactions as well as dipole–dipole interactions are assumed to dominate the self-assembly.

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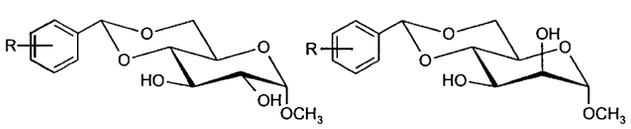
Results and discussion

Synthesis

The preparation of the non-nitro derivatives has been reported elsewhere.[17b,e] The condensation of the C-4 and C-6 hydroxy groups with various nitrophenylbenzaldehydes was carried out with sulfuric acid as catalyst in dimethyl sulfoxide as solvent. The 4,6-*O*-*o*-, *m*- and *p*-nitrobenzylidene protected derivatives of α-glucose (**2**, **3** and **4**), respectively and methyl 4,6-*O*-(*p*-nitrobenzylidene)-α-D-mannopyranoside (**6**) were obtained in moderate yields (Scheme 1). The identity of all compounds was proven by ^{1}H-NMR spectroscopy and elemental analyses. As expected, the nitro-substitution induces a higher polarity compared to the non-nitro compounds. This is reflected by increased melting points. For α-D-glucose the unsubstituted derivative melts at 164.6–166.6 °C,[17e] whereas the nitro analogues show gradually increasing melting points (*o*-NO_2 (**2**): 165.3–168.0 °C; *m*-NO_2 (**3**): 182.6–184.2 °C; *p*-NO_2 (**4**): 210.2–211.7 °C). The same trend is observed for α-D-manno-derivatives (**5**: mp = 149.3–150.0 °C,[17e] **6**: mp = 185.4–186.6 °C). One may thus expect that the interaction between the nitro-substituted phenyl groups is intensified to influence the gel formation.



1 R = H
2 R = *o*-NO_2
3 R = *m*-NO_2
4 R = *p*-NO_2

5 R = H
6 R = *p*-NO_2

Scheme 1 Sugar-integrated gelators investigated.

Gelation properties

The gelation properties have been tested in 28 different solvents. The gelation test was carried out as follows: the gelator (2.4–3.5 mg) was mixed in a close capped test tube with the appropriate amount of solvent (80–110 μl) to result in a concentration of 3 wt/vol% and the mixture was heated until the solid was dissolved. By this procedure the solvent bp becomes higher than that under standard atmospheric pressure. The sample vial was cooled in air to 25 °C, left for 1 h at this temperature and then turned upside down. When the gelator formed a clear or slightly opaque gel by immobilising the solvent at this stage, it was denoted by a "G" in Table 1. Some solutions gelled at a gelator concentration below 1 wt%. The corresponding samples are marked with a "*". The comparison of non-nitro and nitro-derivatives reveals a significant shift in the gelation spectrum. The presence of the nitro group in the *p*-position induces a strong ability to gelate polar solvents and goes along with decreasing ability to gelate nonpolar solvents. 1-*O*-Methyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**5**) can gelate alkanes (entries 1–3 and 5), aromatics like toluene, *p*-xylene and diphenyl ether (entries 7, 8 and 13) as well as carbon disulfide, triethylsilane and water (entries 11, 17 and 28). Its *p*-nitro-analogue **6** does not gelate alkanes and triethylsilane (entries 1–3 and 17) but retains the gelation ability for toluene, *p*-xylene, carbon disulfide, diphenyl ether and water (entries 7, 8, 11, 13 and 28). Additionally, **6** can gelate benzene, carbon tetrachloride, *n*-decanol, glycerol (entries 6, 10, 25 and 26) and partially gelates hexanoic acid (Gp: entry 27). This tendency is strongly reflected by the gelation behaviour of 4,6-*O*-benzylidene and 4,6-*O*-(*p*-nitrobenzylidene)-derivatives of α-glucopyranoside. The non-nitro derivative **1** serves as a gelation agent only in aromatics (entries 6, 7, 8 and 13), carbon tetrachloride (entry 10) and tetraethoxysilane (entry 18) at 1 wt/vol%. On the other hand, the *p*-nitro-analogue **4** shows additional gel formation in carbon disulfide, C_3 to C_{10} alcohols (entries 21–25), glycerol (entry 26), hexanoic acid (entry 27) and water (entry 28) mainly at 3 wt/vol%. No gelation can be observed in tetraethoxysilane. These results clearly substantiate that the presence of a nitro substituent in the *p*-position transforms gelator **1** for nonpolar solvents into more versatile gelator **4** useful not only for nonpolar solvents but also for polar and protic solvents. It is particularly worthy of note that **4** is able to gelate even water. Also the position of the nitro-substituent significantly affects the gelation potential. While the *p*-nitro-derivative **4** shows, compared with **1**, the potential to gelate additional solvents, the presence of the nitro-group in the *ortho*- and *meta*-position results in a drastically decreased gelation ability. The *o*-nitro-derivative **2** shows gel formation only in *p*-xylene, carbon tetrachloride and carbon disulfide (entries 8, 10 and 11) and is soluble in C_1–C_6 alcohols (entries 19–23) but precipitates in higher alcohols, benzene and toluene (entries 6, 7, 24 and 25). In contrast, 1-*O*-methyl-4,6-*O*-(*m*-nitrobenzylidene)-α-D-glucopyranoside (**3**) gelates only diphenyl ether and C_3 to C_{10}-alcohols (entries 13, 21–25). Partial gel formation (Gp) is observed in carbon disulfide (entry 11). These results imply that "bifunctionality" in the sugar-integrated gelators is observed only for the introduction of a nitro-group into the *para*-position.

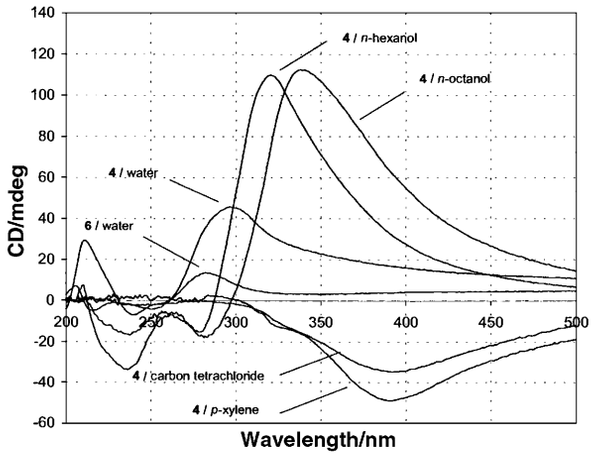


Fig. 1 CD-spectra of gels prepared from **4** in water (0.5 wt/vol%), *n*-octanol (3.0 wt/vol%), *n*-hexanol (3.0 wt/vol%), carbon tetrachloride (0.5 wt/vol%), *p*-xylene (1.0 wt/vol%) and **6** in water (1.0 wt/vol%). Since the thickness of the gel samples is not adjustable, the ordinate shows the reading values (mdeg).

CD-spectroscopy

To characterise the mode of aggregation in the organogel systems, CD spectra of the organogels were measured for different solvents (Fig. 1). In the CD spectra of **4** in water, *n*-hexanol and *n*-octanol the $\lambda_{\theta=0}$ values appear at 260 nm (absorption spectrum: $\lambda_{max} = 268$ nm), 287 nm (absorption spectrum: $\lambda_{max} = 265$ nm) and 297 nm (absorption spectrum: $\lambda_{max} = 263$ nm), respectively. In the CD-spectrum of **6** in water, the CD exhibits a $\lambda_{\theta=0}$ value of 261 nm (absorption spectrum: $\lambda_{max} = 266$ nm). Although there is a slight mismatch between the CD $\lambda_{\theta=0}$ and the absorption λ_{max} in the **4**–*n*-hexanol and **4**–*n*-octanol gels, these bands can be assigned (judging from their spectral shape similarity) to the exciton-coupling bands. All spectra show a positive first Cotton effect and a negative second Cotton effect, suggesting that the *p*-nitrophenyl dipoles are orientated in a clockwise direction (*i.e.* (*R*)-chirality).[8] In contrast, the gels of compound **4** in *p*-xylene and carbon tetrachloride show only a negative absorption maximum without a Cotton effect at $\lambda_{max} = 389$ nm and 392 nm, respectively. In all cases, it was confirmed that the contribution of linear dichroism (LD) to the true CD spectra is negligible. The CD data support the view that the aggregation mode of **4** in polar

Table 1 Organic solvents tested for gelation for **1**, **2**, **3**, **4**, **5** and **6**[a]

Entry	Organic solvent	**1**	**2**	**3**	**4**	**5**	**6**
	Group I						
1	*n*-Hexane[b]	P_S*	P*	P_S*	P_S*	G*	P_S*
2	*n*-Heptane[b]	P_S*	P*	P_S*	P_S*	G*	P_S*
3	*n*-Octane[b]	P_S*	P*	P_S*	P_S*	G*	P_S*
4	Cyclohexane[b]	P_S*	P*	P_S*	P_S*	P_S*	P_S*
5	Methylcyclohexane[b]	P_S*	P*	P_S*	P_S*	G*	P
6	Benzene[b]	G	P	P	G*	P_S*	G*
7	Toluene[b]	G*	P	P*	G*	G*	G*
8	*p*-Xylene[b]	G*	G*	P_S*	G*	G*	G*
9	Nitrobenzene[b]	S	S	S	S	S	S
10	Carbon tetrachloride[b]	G*	G*	P*	G*	P	G*
11	Carbon disulfide[c]	P*	G*	Gp*	G*	G*	G*
12	Diethyl ether[b]	S*	P*	P*	I*	S*	S*
13	Diphenyl ether[b]	G	Gp	G	G*	G	G*
14	Ethyl formate[b]	S	S	P	S	S	S
15	Methyl acetate[b]	S	S	S	S	S	S
16	Triethylamine	S*	S	S*	S*	S	S
17	Triethylsilane	P_S*	P	P_S*	P_S*	G*	P_S
18	Tetraethoxysilane	G*	S	P*	P	S	S
	Group II						
19	Methanol	S	S	S	P	S	S
20	Ethanol	S	S	P	P_S	S	P_S
21	*n*-Propanol	P	S	G	G	S	P_S
22	*n*-Butanol	P	S	G	G	S	P_S
23	*n*-Hexanol	S	S	G	G	S	S
24	*n*-Octanol[b]	S	P	G	G	S	S
25	*n*-Decanol	P_S	P	G	G*	S	G
26	Glycerol	S	S	S	G	S	G
27	Hexanoic acid	S	S	Gp	G	S	Gp
28	Water	P_S	P*	P*	G*	G	G*

[a] 3.0 wt/vol%, * = 1.0 wt/vol%, G = gel, Gp = partial gel, P_S = self-supporting precipitate, P = precipitation, S = solution, I = insoluble. [b] Dried over molecular sieves 4 A. [c] Dried over anhydrous magnesium sulfate.

Table 2 Solvent mixtures tested for gelation of **4** (1 wt/vol%)[a]

vol/vol	*p*-Xylene–*n*-decanol[b]	*p*-Xylene–CCl_4[c]	Water–ethanol[b]
10 : 90	Gp*	G*	G*
20 : 80	P*	G*	G*
30 : 70	P*	G*	P_S*
40 : 60	P*	G*	S*
50 : 50	S*	G*	S*
60 : 40	S*	G*	S*
70 : 30	S*	G*	S*
80 : 20	P*	G*	S*
90 : 10	S*	G*	S*

[a] G* = gel, P_S = self-supporting precipitate, P = precipitation, S = solution. [b] After 1 d. [c] After 1 h.

solvents like water and alcohols is somewhat different from that in nonpolar solvents such as aromatics and carbon tetrachloride. In the case of the polar solvents the type of solvent seems to affect the aggregation mode as indicated by the shift in the $\lambda_{\theta=0}$ values and the CD maxima (**4**: water λ_{max} = 296 nm; *n*-hexanol λ_{max} = 320 nm; *n*-octanol λ_{max} = 337 nm) dependent on different solvents. These findings suggest that the orientation modes of *p*-nitrophenyl dipoles are sensitively affected by the polar solvents.

Different aggregation modes

The foregoing results imply that **4** has the ability to gelate different solvent types by different modes of aggregation. To check the assumption solvent mixtures were tested. Table 2 presents the results of gelation experiments in solvent mixtures of *p*-xylene–*n*-decanol, *p*-xylene–carbon tetrachloride and water–ethanol for **4** at 1 wt/vol%. If the supposition of different aggregation modes is correct, mixtures of different solvent types should not be gelated, whereas mixtures of similar solvent types are supposed to show the gelation effect. A mixture of 'different solvents' such as *p*-xylene with *n*-decanol containing 1 wt/vol% of **4** shows only a partial gel formation for the ratio of 1 : 9 vol/vol. In all other mixtures the monosaccharide **4** is soluble or precipitates. In contrast, mixtures of similar nonpolar solvents like *p*-xylene and carbon tetrachloride are gelated by compound **4** in every mixing ratio. Additionally, gel-formation in water–ethanol mixtures occurs up to an ethanol content of 20 vol%. Although compound **4** shows the formation of a self-supporting precipitate at a concentration of 1 wt/vol% (P_S, entry 20, Table 1), the similar polarity compared with water permits the inclusion of ethanol molecules in the water–gel-network.

Previous investigations revealed that the self-controlled assembly of 1-*O*-methyl-4,6-*O*-benzylidene monosaccharides is driven by the establishment of rigid, strong and highly directional hydrogen-bonds.[17b] However, in water and alcohols solvent molecules can act as competing hydrogen-bond donors and acceptors and therefore suppress the self-aggregation mechanism based on the hydrogen-bonding interaction. Consequently, no gel formation could be observed in these solvents. To explain the exceptional gel formation ability of the nitro-substituted compounds, a different aggregation mode based on hydrophobic effects can be assumed. Due to the highly polarised nitro group, additional attractive electrostatic interactions by coupling of dipole transition moments must be taken into account. Scheme 2 represents the proposed different aggregation modes for the *p*-nitro derivatives **4** and **6** in polar and nonpolar solvents. In the latter ones the assembly is driven by the establishment of hydrogen-bonds into highly-ordered one-dimensional aggregates. Although somewhat more disordered, these aggregates are supposed to be not so "wet" with solvent molecules and display more or less crystal-like character.[6,8,10,18] In polar solvents an assembly to one-dimensional aggregates mediated by solvophobic effects and dipole–dipole interactions

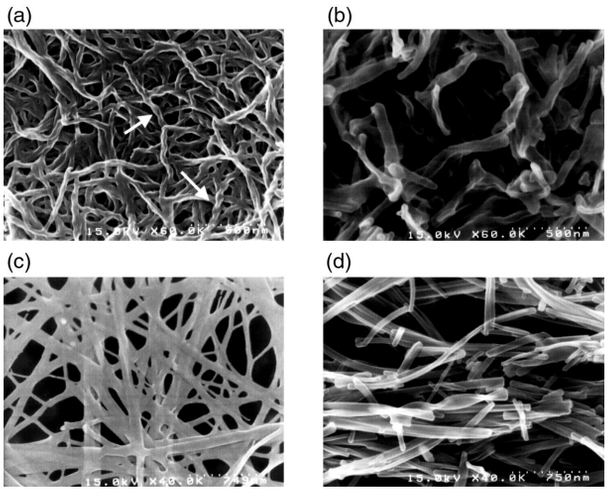
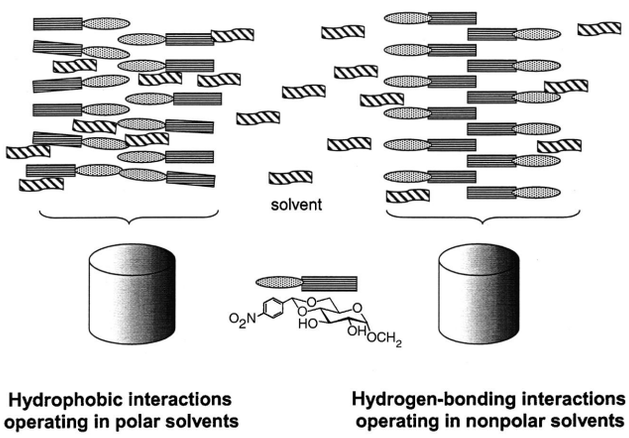


Fig. 2 SEM pictures of **4** and **6**. (a) **6** prepared from water [1% (wt/vol)]; (b) **6** from carbon tetrachloride [0.75% (wt/vol)]; (c) **4** prepared from water [0.5% (wt/vol)]; (d) **4** from carbon tetrachloride [0.5% (wt/vol)].



Scheme 2 Proposed model for different aggregation modes of **4** in polar and nonpolar solvents.

seems to be reasonable. Since no direct evidence for a π–π-stacking interaction of the *p*-nitrophenyl groups in the **4**–water gel could be obtained by applying UV and ^{1}H-NMR spectroscopy in the sol and gel states, weaker and more disordered hydrophobic interactions must be considered as the driving force. It is undoubted, however, that the π–π-stacking interaction plays a central role in the fibrous aggregate formation because in these polar solvents the hydrogen bonds among the OH groups are no longer strong enough to maintain the fibrillar structure. The assumed inclusion of solvent molecules is consistent with the different CD spectra in different solvents.

SEM observations

To visually observe the aggregation modes in the organogel systems, the xerogels of **4** and **6** in water and carbon tetrachloride were prepared by a freezing-and-pumping method from their gel phases below the gel–sol transition temperature and SEM pictures were taken.[19] It is clearly seen from Fig. 2 that gelators form a three-dimensional network. The structure of **6** in water (1.0 wt/vol%) features right-handed helical fibers with diameters around 30–50 nm. The observed macroscopic helicity consists of microscopic helicity obtained by CD-spectroscopy (*vide supra*). Here, the molecular orientation is expressed on the macromolecular level. In the more nonpolar solvent carbon tetrachloride (0.75 wt/vol%) **6** creates featureless frizzled fibrils with diameters from 50–100 nm. The water gel formed by **4** at 0.5 wt/vol%, however, does not show such a helical structure. The obtained fibers are connected by junction nodes and exhibit diameters in the range of 50 to 100 nm. Similar to the results obtained from the α-gluco-derivative **6** the gel structure of **4** at 0.5 wt/vol% in carbon tetrachloride shows frizzled fibrils with diameters ranging from 50 to 100 nm. However, a few knots connecting the fibers could be observed. Although the connection of the fibers to a three-dimensional network is considered to be indispensable for a gel structure, the shrinking step induced by the freeze-drying procedure may result in the collapse of the frail 3-D network.

Conclusion

In conclusion this paper demonstrated that the presence of a nitro-substituent in 1-*O*-methyl-4,6-*O*-(*p*-nitrobenzylidene)-α-D-gluco- and mannopyranoside (**4** and **6**) enables these compounds to gelate organic solvents *and* water, in contrast to their non-substituted analogues. Therefore, they establish a new class of gelators that may be called "bifunctional" low molecular weight organogelators. To the best of our knowledge, this is the first example of a low molecular weight gelator capable of forming gels in both nonpolar and aromatic solvents and polar protic solvents including alcohols and water. This improvement in the gelation spectrum can only be obtained with the introduction of nitro-substituents into the *para*-position, whereas *ortho*- and *meta*-substitution causes a drastic decrease in the gelation ability for all solvents. A possible model, that the monomers can undergo self-assembly depending on the type of solvents driven either by a combination of solvophobic effects with dipole–dipole interactions or by the establishment of hydrogen-bonds, was proposed to explain this "bifunctional aggregation ability".

Experimental

General

All compounds were characterised by NMR, UV and MS spectroscopy and elemental analyses.

Gel–sol transition temperatures

The test tube containing the gel was immersed inversely in a thermostated oil bath. The temperature was raised at a rate of 2 °C min^{-1}. Here, the T_{gel} was defined as the temperature at which the gel turned into the sol-phase.

SEM observations

A Hitachi S-900S scanning electron microscope was used for taking the SEM pictures. The gel was prepared in a sample tube and frozen in liquid nitrogen. The frozen specimen was evaporated by a vacuum pump for 10–15 h. The dry sample obtained was shielded with platin. The accelerating voltage of SEM was 5 kV and the emission current was 10 μA.

Apparatus for spectral measurements

^{1}H NMR spectra were measured with a Bruker ARX 300 apparatus. UV spectra were obtained using a JASCO V-570 spectrometer. A Hitachi M-2500 spectrometer was used recording the mass spectra. The SIMS measurements were carried out in a glycerol or 3-nitrobenzyl alcohol (NBA) matrix with xenon as a primary ion. For CD measurements a JASCO J-820 KS spectrometer was used.

Methyl-4,6-*O*-(*o*-nitrobenzylidene)-α-D-glucopyranoside (2)

Methyl-α-D-glucopyranoside (2.00 g, 10.30 mmol) and *o*-nitrobenzaldehyde (3.12 g, 20.60 mmol) were dissolved in DMSO (20 ml), and concentrated sulfuric acid (1100 μl) was added under ice-cooling. The mixture was kept 3 d at room temperature and poured on to saturated aqueous potassium

hydrogen carbonate solution and extracted with ethyl acetate. After drying over magnesium sulfate, the solvent was removed and the residue subjected to column chromatography (ethyl acetate–*n*-hexane 3 : 1) yielding 391 mg (1.20 mmol, 12%) **2** as colourless solid; mp 165.3–168.0 °C (Found: C, 51.60; H, 5.28; N, 4.23. Calc. for $C_{14}H_{17}O_8N$: C, 51.36; H, 5.23; N, 4.28%); R_t (ethyl acetate–*n*-hexane 3 : 1) 0.19; δ_H [300 MHz, $CDCl_3$] 2.24 (d, *J* 9.4, 1 H), 2.57 (s, 1 H), 3.46 (s, 1 H), 3.54 (t, *J* 9.2, 1 H), 3.60–3.73 (m, 1 H), 3.74–3.82 (m, 2 H), 3.91 (t, *J* 9.2, 1 H), 4.27 (dd, *J* 10.9, 16.2, 1 H), 4.81 (d, *J* 3.9, 1 H), 6.15 (s, 1 H), 7.51 (ddd, *J* 9.3, 7.9, 1.5, 1 H), 7.63 (ddd, *J* 8.8, 7.8, 1.2, 1 H), 7.86–7.91 (m, 2 H); λ_{max}[H_2O, log ε] 262 nm (3.43); [SIMS, glycerol] *m*/*z* 328 (64%, MH^+).

Methyl-4,6-*O*-(*m*-nitrobenzylidene)-α-D-glucopyranoside (3)

Compound **3** was prepared in a similar manner to **2** using methyl-α-D-glucopyranoside (2.00 g, 10.30 mmol), *m*-nitrobenzaldehyde (3.12 g, 20.60 mmol), DMSO (20 ml) and concentrated sulfuric acid (1100 µl) for 14 d at room temperature. Yield 3.21 g (9.81 mmol, 95%) **3** as colourless solid; mp 182.6–184.2 °C (Found: C, 51.60; H, 5.21; N, 4.34. Calc. for $C_{14}H_{17}O_8N$: C, 51.36; H, 5.23; N, 4.28%); R_t (ethyl acetate–*n*-hexane 3 : 1) 0.22; δ_H [300 MHz, $CDCl_3$] 2.24 (d, *J* 9.8, 1 H), 2.71 (s, 1 H), 3.47 (s, 1 H), 3.54 (t, *J* 9.2, 1 H), 3.64 (ddd, *J* 13.3, 9.5, 3.9, 1 H), 3.71–3.83 (m, 2 H), 3.94 (t, *J* 9.2, 1 H), 4.27–4.34 (m, 1 H), 4.81 (d, *J* 3.9, 1 H), 5.62 (s, 1 H), 7.55 (t, *J* 8.0, 1 H), 7.83 (d, *J* 8.8, 2 H), 8.20–8.24 (m, 1 H), 8.39 (t, *J* 1.9, 1 H); λ_{max} [H_2O, log ε] 265 nm (3.86); [SIMS, glycerol] *m*/*z* 328 (48%, MH^+).

Methyl-4,6-*O*-(*p*-nitrobenzylidene)-α-D-glucopyranoside (4)

Compound **4** was prepared in a similar manner to **2** using methyl-α-D-glucopyranoside (8.77 g, 45.15 mmol), *p*-nitrobenzaldehyde (13.65 g, 90.30 mmol), DMSO (90 ml) and concentrated sulfuric acid (4.82 ml) for 10 d at room temperature. After column separation the solid was recrystallised from ethyl acetate. Yield: (9.38 g, 44%) **4** as colourless solid; mp 210.2–211.7 °C (Found: C, 51.52; H, 5.16; N, 4.33. Calc. for $C_{14}H_{17}O_8N$: C, 51.36; H, 5.23; N, 4.28%); R_t (ethyl acetate–*n*-hexane 3 : 1) 0.17; δ_H [300 MHz, $CDCl_3$] 2.27 (d, *J* 9.8, 1 H), 2.74 (s, 1 H), 3.47 (s, 1 H), 3.53 (t, *J* 9.2, 1 H), 3.63 (ddd, *J* 13.4, 9.5, 3.9, 1 H), 3.73–3.82 (m, 2 H), 3.93 (t, *J* 9.2, 1 H), 4.32 (dd, *J* 8.9, 3.3, 1 H), 4.81 (d, *J* 3.9, 1 H), 5.61 (s, 1 H), 7.68 (d, *J* 8.8, 2 H), 8.22 (d, *J* 8.8, 2 H); λ_{max} [H_2O, log ε] 266.2 (3.88); [SIMS, glycerol] *m*/*z* 328 (11%, MH^+).

Methyl-4,6-*O*-(*p*-nitrobenzylidene)-α-D-mannopyranoside (6)

Compound **6** was prepared in a similar manner to **2** using methyl-α-D-mannopyranoside (1.00 g, 5.15 mmol), *p*-nitrobenzaldehyde (1.65 g, 10.92 mmol), DMSO (10 ml) and concentrated sulfuric acid (550 µl) for 3 d at room temperature. Yield 426 mg (1.30 mmol, 25%) of **6** as a colourless solid, mp 185.4–186.7 °C (Found: C, 51.74; H, 5.31; N, 4.28. Calc. for $C_{14}H_{17}O_8N$: C, 51.36; H, 5.23; N, 4.28%); R_t (ethyl acetate–*n*-hexane 3 : 1) 0.38; δ_H [300 MHz, $CDCl_3$] 4.41 (s, 3 H), 3.77–4.15 (m, 5 H), 4.31 (dd, *J* 3.9, 2.3, 1 H), 4.78 (s, 1 H), 5.64 (s, 1 H), 7.68 (d, *J* 8.8, 2 H), 8.23 (d, *J* 8.8, 1 H); λ_{max} [H_2O, log ε] 266.0 (3.89); [SIMS, glycerol] *m*/*z* 328 (25%, MH^+).

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