ChemistrySelect

Research Article
doi.org/10.1002/slct.202300213

Chemistry Europe
European Chemical Societies Publishing

www.chemistryselect.org

Alkylboronate β-Phenylglucoside versus Phenylboronate β-Alkylglucoside Organogelators

Andreas D. Ludwig,[a] Viktoriia Gorbunova,[a] Arnaud Saint-Jalmes,[b] Fabienne Berrée,*[a] and Loïc Lemiègre*[a]

Low molecular weight organogelators provide useful materials which have already found applications in various fields. Recently, phenylboronate alkylglucosides have become new members of this type of organogelators providing water-sensitive gels. This work is focused on the impact of the position of alkyl and phenyl moieties within this type of structures. Thus, alkylboronate phenylglucoside and alkylboronate alkylglucoside counterparts were synthesized and studied. Organogels obtained in toluene and ethyl myristate were characterized by rheology and electron microscopy. In addition, we also determined the disruption rates of such organogels upon addition of a small amount of water. Alkylboronate alkylglucosides did not induce gelation of the tested solvents but all derivatives bearing a phenyl ring either on the boronate function or on the glucoside unit came out as good organogelators. However, alkylboronates were found to have higher water sensitivities than phenyl counterparts. Thus, this work has enlarged the scope of glucoside-boronate organogelators and their water sensitivity which can represent useful materials in drug delivery systems for example.

Introduction

The immobilization of a solvent into a matrix of fibres[1] is a well-known process which has numerous applications in various fields.[2] Among such gels, physical organogels consist in the formation of fibres through a self-assembling process involving weak non-covalent bonds (π-π, vdW interactions, hydrogen network for instance). Those gels can then afford intriguing properties leading to stimuli-responsive material.[3] Among this category of organogels, those formed through the self-assembly of small molecules (LMWOG) are even more challenging. Indeed, such organogelators require a well-defined balance between solubility and self-assembling abilities to form long entangle fibres responsible for the gelation.[4] Numerous LMWOGs have already been described which mostly originate from peptides, fatty acids, and sugars. Carbohydrate-based organogelators represent an important family combining numerous structures and gel properties.[5] Chemical modifications of these scaffolds with alkyl chains, aromatic rings, amide/urea functions usually furnish the required weak bonds (π-π vdW interactions, hydrogen bonding) that favour the self-assembly and the subsequent gelation process. Our research group has recently broadened this family with additional sugar-boronate derivatives[6] that mimic the well-known benzylidene counterparts.[7] We already demonstrated that the substitution of the acetal moiety (benzylidene) with a boronate function has a relatively small impact on the gelation properties of several organic solvents. However, the boronate function added a water-sensitive feature to those organogels. Indeed, the electrophilic boronate function is sensitive to nucleophiles in general and to water in particular. Within this context, one can expect that both gelation properties and water sensitivity might be impacted by the molecular structure of these sugar-boronate organogelators. Thus, we embarked on the comparison of our first family (phenylboronate β-alkylglucosides) with alkylboronate β-phenylglucosides, alkylboronate β-alkylglucosides and phenylboronate β-phenylglucoside (Figure 1). We described herein the synthesis of these new series of compounds along with their gelation properties in organic solvents and the physicochemical characterization of the corresponding organogels (Rheometry, SEM, water sensitivity).

Results and Discussion

Synthesis. The synthetic pathway applied for the preparation of alkylboronate **1**–**6** started with the commercially available β-alkyl or β-phenylglucosides which were esterified in the presence of the corresponding alkyl boronic acid (*n*-butyl or *n*-octyl). The reaction requires the ongoing removal of the water molecules produced during the esterification to displace the equilibrium towards the desired product. Solvent-free Kugelrohr distillations were particularly suitable to produce alkylboronates **1**–**6** in good yields (78–99%) (Scheme 1). Sometimes a treatment with diisopropylether was necessary to clean-up the reaction and obtained pure compounds without additional purification. Indeed, addition of this apolar solvent on the reaction mixture permitted to finish the esterification process

[a] *Dr. A. D. Ludwig, V. Gorbunova, Dr. F. Berrée, Dr. L. Lemiègre*
Univ Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR – UMR6226, F-35000 Rennes, France
E-mail: fabienne.berree@univ-rennes1.fr
loic.lemiegre@ensc-rennes.fr

[b] *Dr. A. Saint-Jalmes*
Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) – UMR 6251, F-35000 Rennes, France

Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.202300213

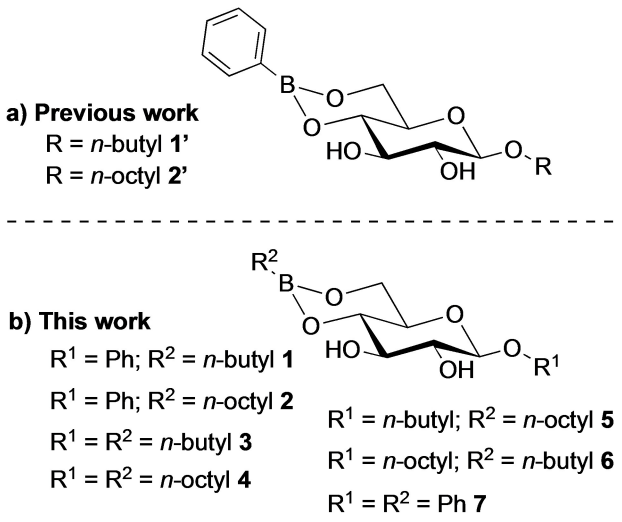
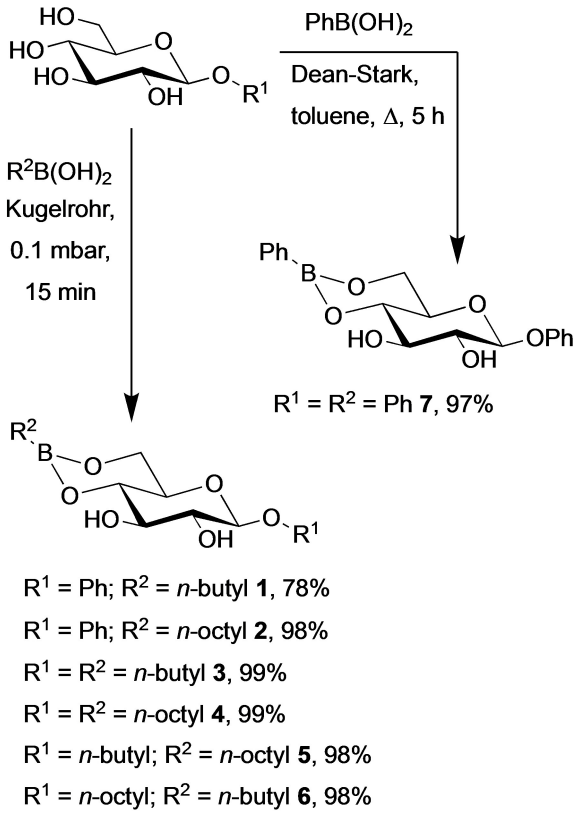


Figure 1. a) Phenylboronate β-alkylglucoside **1'**–**2'**(previous work),[6a] b) Alkylboronate β-phenylglucosides **1**–**2**, alkylboronate β-alkylglucosides **3**–**6** and phenylboronate β-phenylglucoside **7** (this work).



Scheme 1. Synthesis of sugar-boronate derivatives **1**–**7**.

in few minutes, the pure compound was then recovered by filtration. For the phenylboronate β-phenylglucoside **7**, this solvent-free condition did not permit a sufficiently clean reaction, mainly due to a poor mixing of the two starting powders. The esterification in toluene at reflux equipped with a Dean-Stark apparatus solved the problem. After evaporation of the solvent, the desired compound **7** was obtained in an excellent yield (97%). All molecular structures were confirmed by NMR and mass spectrometry analysis.

Gelation ability. This new series of sugar-boronates in hands, we evaluated their gelation abilities in five representative solvents (toluene, cyclohexane, ethyl myristate, ethyl acetate, chloroform). Ethyl myristate is an interesting biocompatible solvent which is relevant for further applications in biomedical or cosmetics for instance.[2c,8] The results and MGC (Minimal Gelation Concentration) are gathered in Table 1. Note that sugar-boronates **3**–**6** equipped with alkyl chains only, led to solutions with most of the solvent used. Among them **3** gave also a partial gel in cyclohexane (less than half of the solvent was gelled) and a precipitate in ethyl myristate. However, compounds **1**–**2** and **7** were suitable gelators for toluene with minimal gelation concentrations ranging from 7 to 15 mg mL^{-1} which are similar or slightly lower than those obtained with the phenylboronate counterparts **1'**–**2'**.[6a] Interestingly, whereas the phenylboronate β-butylglucoside **1'** gave a gel in cyclohexane, boronate **1**–**2** and **7** did not permit to obtain any gel with this solvent but precipitate or insoluble materials instead. Ethyl myristate was gelled with both alkylboronate β-phenylglucosides **1**–**2** again with a lower MGC for the butyl derivative **1**. However, the phenyl derivative **7** was insoluble in this solvent. A clear conclusion raising from this study is the specific need of an aromatic ring on the sugar-boronate structure to obtain gels. It points out the importance of aromatic-aromatic interactions between gelators within the self-assembly of such molecules.[5b,6a]

Gel characterization. We investigated the physicochemical characterizations of the five gels by rheometry and electron microscopy. Rheometry experiments were carried out with gels obtained with boronates **1** in toluene, and **2** in toluene and in ethyl myristate (Figure 2). Unfortunately, the other gels were not strong enough to be characterized by rheometry. At low strain, all materials revealed storage moduli greater than loss moduli which confirmed the formation of gels (Table 2 and see also frequency dependent experiment, Figure S16 in SI). In toluene, boronates **1** and **2** gave similar G′ and G″. The difference is much more visible considering the resistance of the gels to deformation. Indeed, the octyl derivative **2** provided a greater resistance to deformation with about a ten times larger yield strain of 20% (the strain above which the gel gets irreversibly deformed with G″ becoming bigger than G′). In

Table 1. Gelation assays with boronates **1**–**7**.[a]

Boronate	Toluene	Cyclohexane	Ethyl myristate	AcOEt	$CHCl_3$
1	G^T 8	P	G^T 7	S	S
2	G^T 15	I	G^T 15	S	S
3	S	G^P	P	S	S
4	S	S	S	S	S
5	S	S	S	S	S
6	S	S	S	S	S
7	G^T 10	I	I	S	S

[a] I: Insoluble; S: Soluble; P: Precipitate; G^P: Partial gel; G^T: Translucent gel; Values indicate minimum gelation concentrations (MGC) in mg mL^{-1}.

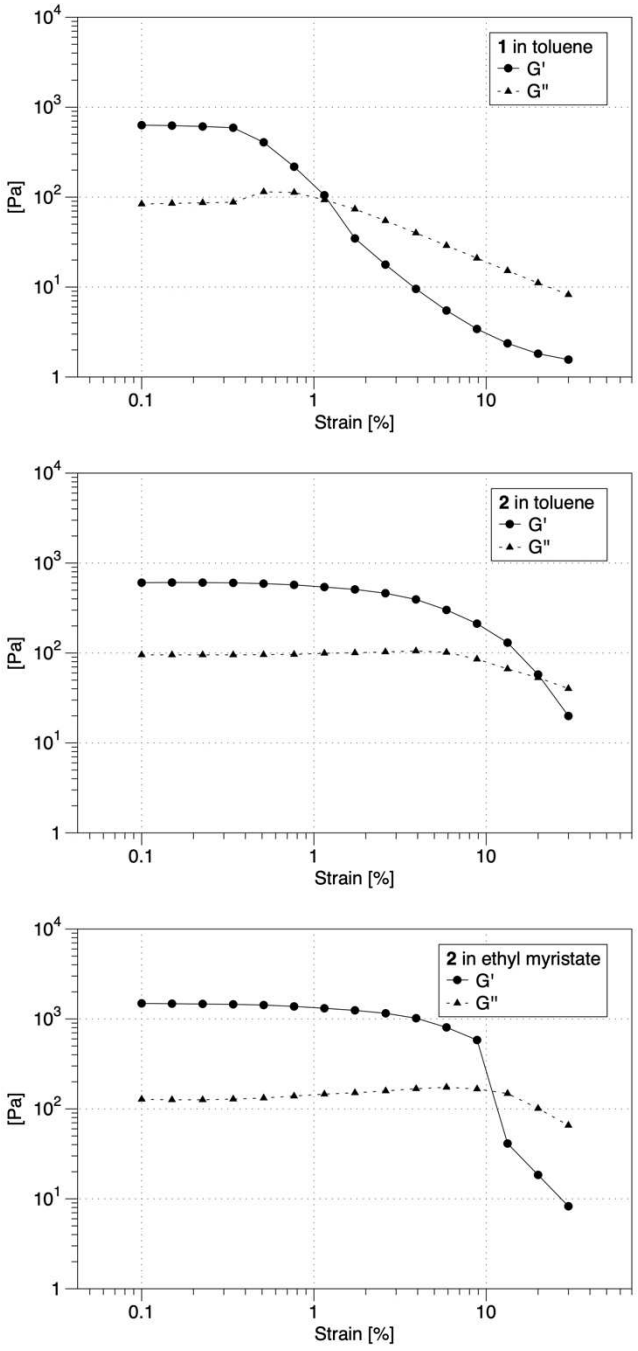


Figure 2. Storage modulus (G′, full line) and loss modulus (G″, dashed line) against strain % of organogels obtained with boronates **1**–**2** in toluene or ethyl myristate.

ethyl myristate, boronate **2** gave higher moduli compared to toluene and still a relatively high yield strain (10%). Comparison of these results with those obtained with the previous phenylboronate β-alkylgucoside family **1′**–**2′** is interesting to discuss. Indeed, when the alkyl chain and the phenyl ring were interchanged, the butyl derivative **1′** gave greater moduli (G′: 2724 Pa, G′/G″: 12.8) than **1** but still a low yield strain (2%). While the octyl derivative **2′** gave poorer moduli values (G′: 753 Pa, G′/G″: 2.2) than **2** but still a large yield strain (30%). Similar comparison can be made for gels formed in ethyl myristate, **2** provided higher moduli values than its interchanged counterpart **2′** (G′: 1075 Pa, G′/G″: 3.7) but a similar yield strain (10 and 15% respectively). Interestingly, these results show that the position of the phenyl ring and the alkyl chain has a limited influence on the yield strain but a great impact on the G′ moduli. It is also noteworthy that the variations of moduli are opposite when comparing butyl chain derivatives and octyl chain ones. Indeed, within the alkyboronate family, the butyl chain gave better gelation properties than the octyl derivative. However, for the phenylboronate counterparts, we observed the reverse situation; the octyl derivative giving better gelation properties than the butylboronate.

Scanning electron macroscopy (SEM) images were recorded after lyophilization of toluene-based gels with compounds **1**–**2**. These images permit to observe the result of the self-assembly of this organogelator within the gels. The xerogel obtained with the butyl derivative **1** gave fibres of 1 μm width arranged in bundles (Figure 3, top). However, the *n*-octyl counterpart **2** provided images revealing a dense fibre network where it was difficult to identify the fibres (Figure 3, bottom).

Water sensitivity. Another specific behaviour of such sugar-boronate organogelators is their ability to be hydrolysed leading then to the disruption of the corresponding gels. In fact, the hydrolysis of the boronate function leads back to the two starting materials (glucoside and boronic acid) which are not organogelator themselves. Thus, we evaluated the impact of the position of both the alkyl chain and the phenyl ring on these sugar-boronate structures, on the disruption of the gels upon water addition. These water sensitivity assays were performed on toluene-based gels formed in the presence of **1**–**2** and **7** and their interchanged counterparts **1′**–**2′**. Water (5% v/v) was added on the top of the gels in a tube and the time needed to disrupt the wholeness of each gel was determined (Table 3). The phenylboronate phenylglucoside **7** got disrupted

Table 2. Main data extracted from rheometry analysis at low strain[a] and yield strain.

Compound	Solvent	G′ [Pa]	G″ [Pa]	G′/G″	Yield strain [%]
1 (*n*-butyl)	Toluene	631	84	7.5	1
2 (*n*-octyl)	Toluene	606	95	6.4	20
2 (*n*-octyl)	Ethyl Myristate	1490	128	11.6	10

[a] At strain < 1%, 1 Hz frequency.

Table 3. Disruption time upon addition of water on toluene-based gels (5% v/v).

Compounds	Time [h]
1 (R^1 = Ph, R^2 = *n*-butyl)	2
2 (R^1 = Ph, R^2 = *n*-octyl)	48
7 (R^1 = R^2 = Ph)	1
1′ (R^1 = *n*-butyl, R^2 = Ph)	3
2′ (R^1 = *n*-octyl, R^2 = Ph)	/[a]

[a] No hydrolysis after one week.

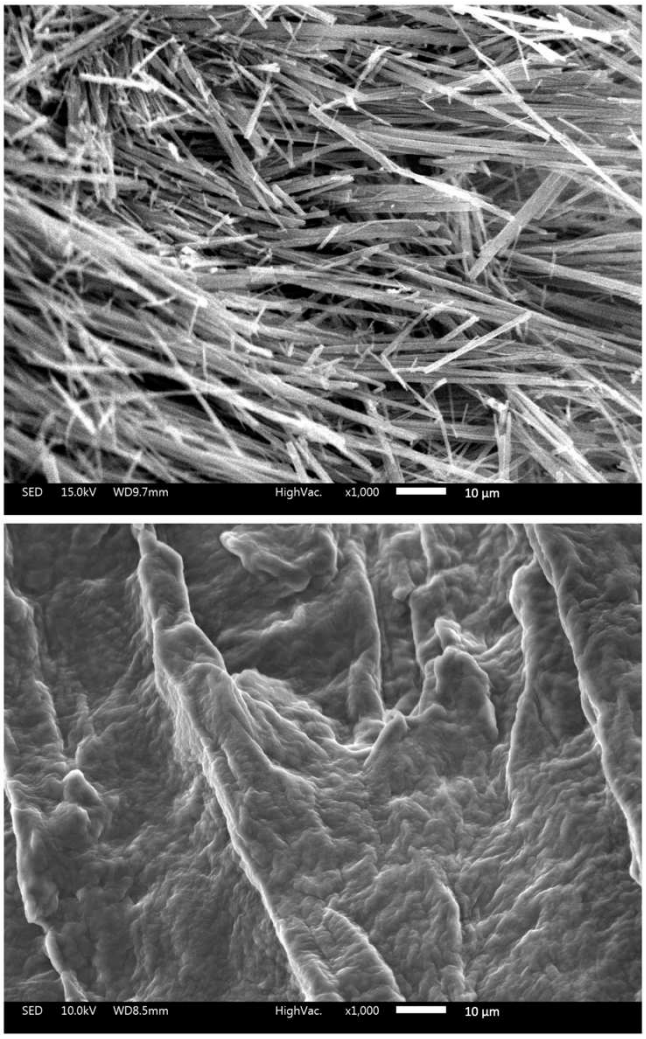


Figure 3. SEM images obtained from corresponding xerogels, top: from *n*-butylboronate β-phenylglucoside **1** in toluene at MGC and bottom: from *n*-octylboronate β-phenylglucoside **2** in toluene at MGC. Scale bar: 10 µm.

in 1 h only. This less cohesive gel is thus more sensitive to the water penetration than **1**–**2** and **1′**–**2′**. The *n*-butyl derivatives **1**–**1′** led to higher water sensitivity than the *n*-octyl counterparts **2**–**2′** confirming the fact that more hydrophobic organogelators are less water-sensitive. The comparison of regioisomers **1**–**1′** on the one side and **2**–**2′** on the other side provides a clear influence of the place of both the aromatic ring and the alkyl chain on the organogelator structures. Indeed, both for *n*-butyl and *n*-octyl, the derivatives bearing the alkyl chain on the boronate function (**1**–**2**) had a much higher water sensitivity than the regioisomers **1′**–**2′**. Therefore, the phenylboronates have a lower water sensitivity compared to alkylboronate.

Conclusion

In conclusion we synthesized new members of organogelators based on a sugar-boronate structure bearing alkyl chains or a phenyl ring alternatively on the boronate function or on the sugar unit. Only compounds bearing a phenyl ring led to gelation in two solvents (toluene and ethyl myristate), keeping those with alkyl chains only as solution in these solvents. It means that an aromatic ring is a requirement for sugar-boronate derivatives to behave as organogelators. Within our comparative study, the regioisomers bearing the alkyl chain on the boronate function provided a higher water sensitivity than their interchanged regioisomers where the alkyl chain and the phenyl ring were inverted. Therefore, this study added new clues on the impact of the structure of these organogelators on their gelation capacity and, on the viscoelastic properties and the water sensitivity of the so-formed gels. All together these two series of regioisomer organogelators afford a wide range of gel disruption rates upon addition of a small amount of water. Then, it would allow new possibilities for the development of controlled water-sensitive drug delivery system for example.

Experimental Section

General. ^{1}H NMR spectra (300 MHz, 400 MHz), ^{13}C NMR (75 MHz, 101 MHz) and ^{11}B (96, 128 MHz) were recorded on Bruker AC 300 and AC 400 spectrometers. Chemical shifts are given in ppm and coupling constants *J* in Hz. Multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. The carbon bearing the boron atom was not observed due to the quadrupolar relaxation mechanism of ^{11}B nucleus. High-resolution mass spectra (HRMS) were recorded, either on a Bruker MaXis 4G, an Agilent 6510, or a Thermo Fisher Q-Exactive spectrometer (Centre Régional de Mesures Physiques de l'Ouest, Rennes) using positive ion Electron-Spray ionization techniques. Melting points were measured on a melting point apparatus Stuart SMP10 and are uncorrected.

General procedure for the synthesis of boronates 1–6. In a 25 mL round bottom flask, alkylglucoside (0.3 mmol) and alkylboronic acid (0.3 mmol) were added. The mixture was then stirred in a kugelrohr distillation apparatus at 90 °C; under 0.1 mbar for 15 min to give the product pure enough to make gels. Compounds were treated with diisopropylether when necessary.

General procedure for the synthesis of boronate 7. In a 25 mL round bottom flask, glycoside (0.3 mmol) and boronic acid (0.3 mmol) were added. Toluene (15 mL) was then added, and the mixture was heated under stirring at reflux for 5 hours equipped with a Dean-Stark apparatus. The toluene was evaporated under reduced pressure to give the pure product. Compounds were then treated with diisopropylether when necessary.

Phenyl-β-D-glucopyranoside 4,6-(*n*-butyl)boronate 1. Yield: 78%. White solid; mp = 209–211 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 2H), 7.12–6.99 (m, 3H), 5.03 (d, *J* = 7.1 Hz, 1H, H_1), 4.15 (dd, *J* = 10.4, 5.3 Hz, 1H, H_6), 3.85 (t, *J* = 10.3 Hz, 1H, H_6), 3.78–3.51 (m, 4H, $H_{2\text{-}5}$), 2.87 (d, *J* = 1.5 Hz, 1H, OH), 2.70 (d, *J* = 2.3 Hz, 1H, OH), 1.42–1.19 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.76 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 129.8, 123.5, 117.0, 101.4 (C_1), 75.1 (C_3), 74.0 (C_4), 74.0 (C_2), 68.8 (C_5), 63.8 (C_6), 26.3, 25.5, 14.1. The carbon α to the boron was not observed. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.2. HRMS (ESI) $(M+Na)^+$ calculated for $C_{16}H_{23}{}^{11}BO_6Na$ 345.1485, found 345.1481.

Phenyl-β-D-glucopyranoside 4,6-(*n*-octyl)boronate 2. Yield: 98%. White solid; mp = 150–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (t,

J=7.8 Hz, 2H), 7.11–7.01 (m, 3H), 5.03 (d, J=7.1 Hz, 1H, H_1), 4.15 (dd, J=10.3, 5.2 Hz, 1H, H_6), 3.85 (t, J=10.3 Hz, 1H, H_6), 3.80-3.64 (m, 3H, $H_{2\text{-}4}$), 3.55 (td, J=9.4, 2.2 Hz, 1H, H_5), 2.92 (brs, 1H, OH), 2.75 (brs, 1H, OH), 1.67-1.23 (m, 12H), 0.88 (t, J=6.4 Hz, 3H), 0.75 (t, J=7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9, 129.8, 123.5, 117.1, 101.3 (C_1), 75.0 (C_3), 74.0 (C_4), 74.0 (C_2), 68.8 (C_5), 63.8 (C_6), 32.6, 32.1, 29.6, 29.4, 24.1, 22.8, 14.3. The carbon α to the boron was not observed. ^{11}B NMR (96 MHz, $CDCl_3$) δ 28.8. HRMS (ESI) $(M+Na)^+$ calculated for $C_{20}H_{31}O_6{}^{11}BNa$ 401.2111, found 401.2106.

***n*-Butyl-β-D-glucopyranoside 4,6-(*n*-butyl)boronate 3**. Yield: 99%. White solid; mp=94–95 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.37 (d, J=7.7 Hz, 1H, H_1), 4.09 (dd, J=10.3, 5.3 Hz, 1H, H_6), 3.90 (dt, J=9.5, 6.8 Hz, 1H, OCH_2), 3.81 (t, J=10.3 Hz, 1H, H_6), 3.67-3.33 (m, 5H, OCH_2, H_2-H_5), 3.09 (d, J=1.8 Hz, 1H, OH), 2.85 (d, J=2.6 Hz, 1H, OH), 1.69–1.51 (m, 2H), 1.47–1.17 (m, 6H), 0.92 (t, J=7.2 Hz, 3H), 0.87 (t, J=7.2 Hz, 3H), 0.73 (t, J=7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 103.3 (C_1), 75.0 (C_4), 74.3 (C_3), 74.2 (C_2), 70.5 (OCH_2), 68.6 (C_5), 63.9 (C_6), 31.8, 26.3, 25.5, 19.2, 14.0, 13.9. The carbon α to boron was not observed. ^{11}B NMR (96 MHz, $CDCl_3$) δ 31.6. HRMS (ESI) $(M+Na)^+$ calculated for $C_{14}H_{27}O_6{}^{11}BNa$ 325.1798, found 325.1794.

***n*-Octyl-β-D-glucopyranoside 4,6-(*n*-octyl)boronate 4**. Yield: 99%. White solid; mp=72–73 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.37 (d, J=7.7 Hz, 1H, H_1), 4.09 (dd, J=10.3, 5.4 Hz, 1H, H_6), 3.86 (dt, J=9.4, 6.9 Hz, 1H, OCH_2), 3.80 (t, J=10.3 Hz, 1H, H_6), 3.67-3.29 (m, 5H, OCH_2, H_2-H_5), 3.03 (d, J=1.7 Hz, 1H, OH), 2.79 (d, J=2.5 Hz, 1H, OH), 1.62 (quint, J=6.8 Hz, 2H), 1.41–1.17 (m, 22H), 0.87 (t, J=6.6 Hz, 6H), 0.72 (t, J=7.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 103.3 (C_1), 75.0 (C_4), 74.3 (C_3), 74.2 (C_2), 70.7 (OCH_2), 68.7 (C_5), 63.9 (C_6), 32.6, 32.1, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 26.0, 24.1, 22.8, 22.8, 14.2, 14.2. The carbon α to boron was not observed. ^{11}B NMR (96 MHz, $CDCl_3$) δ 31.2. HRMS (ESI) $(M+Na)^+$ calculated for $C_{22}H_{43}O_6{}^{11}BNa$ 437.3050, found 437.3045.

***n*-Butyl-β-D-glucopyranoside 4,6-(*n*-octyl)boronate 5**. Yield: 98%. White solid; mp=69–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.37 (d, J=7.7 Hz, 1H, H_1), 4.09 (dd, J=10.4, 5.3 Hz, 1H, H_6), 3.88 (dt, J=9.5, 6.7 Hz, 1H, OCH_2), 3.81 (t, J=10.4 Hz, 1H, H_6), 3.65–3.34 (m, 5H, OCH_2, H_2-H_5), 3.06 (d, J=1.8 Hz, 1H, OH), 2.83 (d, J=2.5 Hz, 1H, OH), 1.67–1.55 (m, 2H), 1.46–1.17 (m, 14H), 0.93 (t, J=7.3 Hz, 3H), 0.87 (t, J=7.0 Hz, 3H), 0.73 (t, J=7.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 103.3 (C_1), 75.0 (C_4), 74.3 (C_3), 74.2 (C_2), 70.4 (OCH_2), 68.6 (C_5), 63.9 (C_6), 32.6, 32.1, 31.8, 29.6, 29.4, 24.1, 22.8, 19.2, 14.2, 13.9. The carbon α to boron was not observed. ^{11}B NMR (96 MHz, $CDCl_3$) δ 31.0. HRMS (ESI) $(M+Na)^+$ calculated for $C_{18}H_{35}O_6{}^{11}BNa$ 381.2424, found 381.2420.

***n*-Octyl-β-D-glucopyranoside 4,6-(*n*-butyl)boronate 6**. Yield: 98%. White solid; mp=66–68 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.37 (d, J=7.7 Hz, 1H, H_1), 4.09 (dd, J=10.3, 5.3 Hz, 1H, H_6), 3.86 (dt, J=9.4, 6.8 Hz, 1H, OCH_2), 3.80 (t, J=10.3 Hz, 1H, H_6), 3.67–3.32 (m, 5H, OCH_2, H_2-H_5), 3.06 (brs, 1H, OH), 2.81 (brs, 1H, OH), 1.62 (quint, J=6.9 Hz, 2H), 1.42-1.23 (m, 14H), 0.87 (t, J=6.9 Hz, 3H), 0.86 (t, J=7.1 Hz, 3H), 0.73 (t, J=7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 103.3 (C_1), 75.0 (C_4), 74.3 (C_3), 74.2 (C_2), 70.7 (OCH_2), 68.6 (C_5), 63.9 (C_6), 31.9, 29.7, 29.5, 29.3, 26.3, 26.0, 25.5, 22.8, 14.2, 14.0. The carbon α to boron was not observed. ^{11}B NMR (96 MHz, $CDCl_3$) δ 34.1. HRMS (ESI) $(M+Na)^+$ calculated for $C_{18}H_{35}O_6{}^{11}BNa$ 381.2424, found 381.2421.

Phenyl-β-D-glucopyanoside 4,6-phenylboronate 7. Yield: 97%. White solid; mp=193–195 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J=7.1 Hz, 2H), 7.46 (t, J=7.5 Hz, 1H), 7.40–7.30 (m, 4H), 7.12–7.04 (m, 3H), 5.08 (d, J=6.1 Hz, 1H, H_1), 4.33 (dd, J=9.6, 4.3 Hz, 1H, H_6), 4.03 (t, J=9.5 Hz, 1H, H_6), 3.92-3.83 (m, 3H, $H_{2\text{-}4}$), 3.69 (td, J=9.2, 2.1 Hz, 1H, H_5), 2.95 (brs, 1H, OH), 2.75 (brs, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0, 134.3, 131.4, 129.8, 127.8, 123.5, 117.1, 101.4 (C_1), 75.1 (C_3), 74.4 (C_4), 74.1 (C_2), 68.9 (C_5), 64.1 (C_6). The carbon α to the boron was not observed. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.1. HRMS (ESI) $(M+Na)^+$ calculated for $C_{18}H_{19}O_6{}^{11}BNa$ 365.1172, found 365.1168.

Gel formation. The gels were prepared by mixing the appropriate amount of gelator into the appropriate organic solvent at various percentages in capped tubes. The tubes were heated at 60 °C (cyclohexane), 80 °C (toluene) or 120 °C (ethyl myristate) for 1 h or until clear solutions were obtained. Clear solutions were then cooled down to room temperature to allow the formation of a gel.

Rheometry. Organogel samples were presented under disc form (4 cm diameter). Rheological measurements were performed on an Anton-Paar MCR301 equipped with an upper plate of 75 mm diameter. The frequency (ω) was fixed to 1 Hz and the amplitude deformation (γ°) was gradually increased from 0 to 50% of shearing. Storage modulus G′ and the loss modulus G″ were obtained at 25 °C.

Scanning electron microscopy (SEM). Metallization by Au/Pd. Scanning Electron Microscopy (SEM) of xerogels were evaluated using the JEOL IT 300 Scanning Electron Microscope. Samples were collected and deposited on a Teflon plot. Each sample was examined using a voltage of 5 or 10 kV. Images were analysed by SMileView software.

Supporting Information Summary

^{1}H, ^{13}C, ^{11}B NMR spectra of each new compound and frequency dependent experiment of a gel in toluene with **2′** can be found in the SI.

Acknowledgements

We acknowledge the Ministère de l'Education Nationale, de la Recherche et de la Technologie. The authors thank F. Gouttefangeas and L. Joanny from the CMEBA (Centre de Microscopie Electronique à Balayage et microAnalyse, Rennes) for assistance in recording the SEM images.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: boronate · glycoside · organogel · self-assembly · water-sensitive

[1] a) M. George, R. G. Weiss, *Acc. Chem. Res.* **2006**, *39*, 489–497; b) S. S. Babu, V. K. Praveen, A. Ajayaghosh, *Chem. Rev.* **2014**, *114*, 1973–2129; c) A. Ajayaghosh, V. K. Praveen, *Acc. Chem. Res.* **2007**, *40*, 644–656.
[2] a) Y. Ohsedo, *Polym. Adv. Technol.* **2016**, *27*, 704–711; b) C. L. Esposito, P. Kirilov, V. G. Roullin, *J. Controlled Release* **2018**, *271*, 1–20; c) S. Uzan, D. Barış, M. Çolak, H. Aydın, H. Hoşgören, *Tetrahedron* **2016**, *72*, 7517–7525; d) R. Swati, K. Ankaj, P. Vinay, *World J. Pharm. Pharm. Sci.* **2015**, *4*, 455–

471; e) K. J. Skilling, F. Citossi, T. D. Bradshaw, M. Ashford, B. Kellam, M. Marlow, *Soft Matter* **2014**, *10*, 237–256; f) C. L. Esposito, V. Tardif, M. Sarrazin, P. Kirilov, V. G. Roullin, *Mater. Sci. Eng. C* **2020**, *114*, 110999.

[3] a) A. Dawn, B. Roy, S. Shinkai, *RSC Smart Mater.* **2015**, *14*, 67–97; b) E. R. Draper, D. J. Adams, in *Chemoresponsive Materials: Stimulation by Chemical and Biological Signals*, The Royal Society of Chemistry, **2015**, pp. 332–363.

[4] a) D. R. Nunes, M. Raynal, B. Isare, P.-A. Albouy, L. Bouteiller, *Soft Matter* **2018**, *14*, 4805–4809; b) J. Bonnet, G. Suissa, M. Raynal, L. Bouteiller, *Soft Matter* **2014**, *10*, 3154–3160; c) M. Raynal, L. Bouteiller, *Chem. Commun.* **2011**, *47*, 8271–8273.

[5] a) J. Morris, J. Bietsch, K. Bashaw, G. Wang, *Gels* **2021**, *7*, 24; b) A. D. Ludwig, F. Berrée, L. Lemiègre, in *Carbohydrate Chemistry, Vol. 45*, The Royal Society of Chemistry, **2022**, pp. 379–415; c) N. Basu, A. Chakraborty, R. Ghosh, *Gels* **2018**, *4*, 52.

[6] a) A. D. Ludwig, A. Saint-Jalmes, C. Mériadec, F. Artzner, O. Tasseau, F. Berrée, L. Lemiègre, *Chem. Eur. J.* **2020**, *26*, 13927–13934; b) A. D. Ludwig, N. Ourvois-Maloisel, A. Saint-Jalmes, F. Artzner, J. P. Guegan, O. Tasseau, F. Berrée, L. Lemiègre, *Soft Matter* **2022**, *18*, 9026–9036.

[7] a) A. M. Vibhute, V. Muvvala, K. M. Sureshan, *Angew. Chem. Int. Ed.* **2016**, *55*, 7782–7785; *Angew. Chem.* **2016**, *128*, 7913–7916; b) F. Ono, K. Ichimaru, O. Hirata, S. Shinkai, H. Watanabe, *Chem. Lett.* **2020**, *49*, 156–159; c) F. Ono, O. Hirata, K. Ichimaru, K. Saruhashi, H. Watanabe, S. Shinkai, *Eur. J. Org. Chem.* **2015**, *2015*, 6439–6447; d) K. Sakurai, Y. Jeong, K. Koumoto, A. Friggeri, O. Gronwald, S. Sakurai, S. Okamoto, K. Inoue, S. Shinkai, *Langmuir* **2003**, *19*, 8211–8217; e) O. Gronwald, S. Shinkai, *Chem. Eur. J.* **2001**, *7*, 4329–4334; f) J. Kowalczuk, M. Bielejewski, A. Lapinski, R. Luboradzki, J. Tritt-Goc, *J. Phys. Chem. B* **2014**, *118*, 4005–4015; g) J. Tritt-Goc, J. Kowalczuk, *Langmuir* **2012**, *28*, 14039–14044; h) A. Chen, L. P. Samankumara, C. Garcia, K. Bashaw, G. Wang, *New J. Chem.* **2019**, *43*, 7950–7961; i) A. Chen, I. S. Okafor, C. Garcia, G. Wang, *Carbohydr. Res.* **2018**, *461*, 60–75; j) G. Wang, A. Chen, H. P. R. Mangunuru, J. R. Yerabolu, *RSC Adv.* **2017**, *7*, 40887–40895; k) J. Morris, P. Kozlowski, G. Wang, *Langmuir* **2019**, *35*, 14639–14650.

[8] K. Peng, N. Preisig, T. Sottmann, C. Stubenrauch, *Langmuir* **2020**, *36*, 12692–12701.

Submitted: January 18, 2023
Accepted: February 2, 2023