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Charge-Transfer Phenomena in Novel, Dual-Component, Sugar-Based Organogels

Arianna Friggeri,[†,§] Oliver Gronwald,[†] Kjeld J. C. van Bommel,[†,§] Seiji Shinkai,*[,†] and
David N. Reinhoudt[‡]

Contribution from the Chemotransfiguration Project, Japan Science and Technology Corporation, Aikawa, Kurume, Fukuoka 839-0861, Japan, and the Chemotransfiguration Project, MESA+ Research Institute, University of Twente, 7500 AE Enschede, The Netherlands

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Abstract: The synthesis of a new saccharide-based gelator (**2**) containing a donor moiety has been described. Gelation experiments of a dual-component gel consisting of a saccharide-based gelator bearing an acceptor group (**1**) and of **2** have been performed in a variety of organic solvents and water. Moreover, gelation tests at different molar ratios of **1** and **2** have been performed in water, octanol, and diphenyl ether. In these last two solvents a gel color change was observed, from colorless to yellow, upon cooling of the sample to room temperature. This phenomenon was further investigated by UV−visible spectroscopy, which revealed the presence of charge-transfer interactions in the gel, in octanol. Temperature-dependence UV spectroscopy confirmed that such interactions occur in the gel but not in the corresponding solution sample. Furthermore, T_{gel} measurements show that dual-component gels of **1** and **2** present increased thermal stability at a 50:50 ratio of the two gelators, in dependence of the solvent. Transmission electron microscopy (TEM) images of the single-component gels in diphenyl ether revealed that they consist of a fibrous network, while the dual-component gel presents a novel, helical, fibrous-bundle structure.

Introduction

Organogels are thermoreversible, viscoelastic materials consisting of low molecular weight compounds self-assembled into complex three-dimensional networks.[1] The aggregation of gelator molecules into fibrous networks is driven by multiple, weak interactions such as dipole−dipole, van der Waals, and hydrogen-bonding interactions.[1] Gelators are thus generally classified according to their driving force for molecular aggregation, into two categories: non-hydrogen bond-based and hydrogen bond-based gelators. Cholesterol derivatives[2] are examples of the former, while amide-, urea-,[3] and saccharide-based[1c,4] compounds fall into the latter category. In our group special attention has been paid to saccharide-based gelators with the aim of synthesizing a large carbohydrate-based gelator library.[5] Gelation ability and strength has been found to correlate significantly with the absolute configuration of the sugar, as well as with the substituents present on the sugar unit.

In recent years organogels have attracted considerable attention due to their numerous industrial applications as well as their interesting supramolecular architectures.[1] In particular, there has been an increasing interest in the development of dual-component gels for the exploitation of new functions inherent to these systems. For practical applications, however, improvement of gel strength and stability are essential. Postpolymerization of gel fibers,[6] and the addition of polymers[7] or hydrogen-bonding guests,[8] have proven to be successful approaches toward gel stabilization. The introduction of metal ions, on the other hand, has been carried out to investigate the sensing and catalysis potentials of gels.[9] Furthermore, two-component gel systems

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* To whom correspondence should be addressed. E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp.

[†] Japan Science and Technology Corporation.

[‡] University of Twente.

[§] Present address: BiOMaDe Technology Foundation, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

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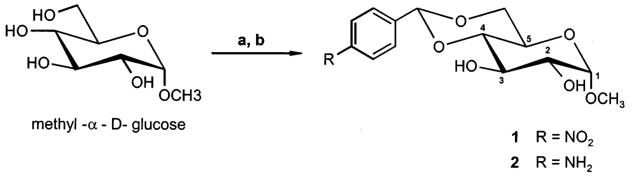
Scheme 1. Synthesis of Gelators **1** and **2**[a]



[a] (a) 2 equiv of p-$NO_2C_6H_4CHO$, H_2SO_4, DMSO, 10 days, rt, 44%; (b) H_2, 1 wt % Pd/C, ethanol, 30 min, 98%.

are also being used to investigate molecular properties/interactions such as chirality[10] and donor−acceptor interactions[11] within gel fibers.[12] To the best of our knowledge, Maitra et al.[11] presented the first and only report on donor−acceptor interactions in organogels, only a few years ago, by doping gels of donor-substituted derivatives with trinitrofluorenone.

In this paper, we present a novel donor−acceptor, sugar-based gelator system in which the simultaneous gelation of two gelators, one containing an acceptor group (**1**) and the other a donor group (**2**), gives rise to charge-transfer phenomena within the gel (Scheme 1). Moreover, these dual-component gels present an increased thermal stability which was found to be strongly dependent on the solvent and on the ratio of the two gelators. Furthermore, transmission electron microscopy (TEM) images of the two-component gel network in diphenyl ether have revealed a novel organogel structure, with a helical motif, that differs greatly from that of the single-component gels in the same solvent.

Results and Discussion

In analogy to the preparation of nonsubstituted methyl 4,6-*O*-benzylidene derivatives,[5] the condensation of the C-4 and C-6 hydroxyl groups with *p*-nitrobenzaldehyde in the presence of sulfuric acid in dimethyl sulfoxide resulted in methyl 4,6-*O*-(*p*-nitrobenzylidene)-α-D-**glucopyranoside (1**) (Scheme 1).[13] Hydrogenation in ethanol with palladium on activated carbon induces the formation of the corresponding amino compound **2** in nearly quantitative yield (98%). As expected, the exchange of the electron-withdrawing nitro substituent with the electron-donating amino substituent induces a high-field shift of the aromatic protons in the ^{1}H NMR (**2**, $\delta_H = 6.49$ and 7.04 ppm; **1**, $\delta_H = 7.68$ and 8.23 ppm). In addition, the UV absorption spectrum in water confirms with a significant blue shift in the absorption maximum from $\lambda_{max} = 266.0$ nm (**1**) to $\lambda_{max} = 239.4$ nm (**2**) the successful transformation. The coupling constants of 1-H ($\delta_H = 4.60$ ppm, d, $J_{1-H,2-H} = 4.2$ Hz) and 2-H ($\delta_H = 4.08$ ppm, dd, $J_{1-H,2-H} = 4.2$ Hz, $J_{2-H,3-H} = 9.3$ Hz) with the neighboring protons prove their axial (1-H) and equatorial (2-H, 3-H) orientation and thus that the gluco configuration of the sugar moiety remained unchanged.

Table 1. Organic Solvents Tested for Gelation of **1**, **2**, and **1**/**2** Mixtures (50:50)[a]

	solvent	**1**	**2**	**1**/**2** mix
		Group I		
1	*n*-hexane[b]	P_s^c	I	
2	*n*-heptane[b]	P_s^c	I	
3	*n*-octane[b]	P_s^c	I	
4	cyclohexane[b]	P_s^c	I	
5	methylcyclohexane[b]	P_s^c	I	
6	benzene[b]	G^c	G^c	P^c
7	toluene[b]	G^c	P^c	P_s^c
8	*p*-xylene[b]	G^c	P^c	P_s^c
9	nitrobenzene[b]	S	P	
10	carbon tetrachloride[b]	G^c	P^c	P^c, G^d
11	carbon disulfide[e]	G^c	G^c	G
12	diethyl ether[b]	I^c	I^c	
13	diphenyl ether[b]	G^c	G^c	G
14	ethyl formate[b]	S	P	
15	methyl acetate[b]	S	S	
16	triethylamine	S^c	P^c	
17	triethylsilane	P_s^c	P^c	
18	tetraethoxysilane	P	P^c	
		Group II		
19	methanol			P
20	ethanol	P_s	P	P
21	*n*-propanol	G	P	S
22	*n*-butanol	G	S^c	S
23	*n*-hexanol	G		S
24	octanol[b]	G	P	G
25	*n*-decanol	G^c		G
26	glycerol	G	S	
27	hexanoic acid	G	reaction	
28	water	G^c	S	S^c

[a] All **1**/**2** mixtures are 3.0% (w/v) unless specified. G = gel, P_S = self-supporting precipitate, P = precipitation, S = solution, I = insoluble. [b] Dried over molecular sieves 4 Å. [c] 1.0% (w/v). [d] 0.5%, 0.25% (w/v). [e] Dried over anhydrous magnesium sulfate.

Table 2. Gelation Tests for Different Molar Ratios of **1** and **2** in Water, Octanol, and Diphenyl Ether, with Corresponding Gel Colors[a]

1:**2**	H_2O (1 wt %)	color	octanol (3 wt %)	color	diphenyl ether (3 wt %)	color
100:0	G	none	G	white[b]	G	none
90:10	G	none	G	white[b]	G	yellow 1
80:20	G	none	WG	yellow 1	G_p	yellow 1
70:30	G	none	WG	yellow 1	G	yellow 1
60:40	G_p	none	WG	yellow 1	G	yellow 1
50:50	S	none	G	yellow 2	G	yellow 1
40:60	S	none	G	yellow 2	G	yellow 2
30:70	S	none	P	yellow 2	G	yellow 2
20:80	S	none	P	yellow 1	G	yellow 2
10:90	S	none	P	yellow 1	G	yellow 2
0:100	S	none	P	white	G^c	none

[a] G = gel; G_p = partial gelation; WG = weak gel. Yellow 1 is a paler yellow than yellow 2. [b] Turbid. [c] 1.0% (w/v).

Gelator **1** can gelate both aromatic solvents, as well as nonaromatic polar solvents, and is also a very good gelator for water, while it performs rather poorly in nonaromatic nonpolar solvents, where it has a tendency to form self-supporting precipitates (Table 1).[13,14] Gelator **2**, on the other hand, has a much more limited solvent gelation range (Table 1). However, mixtures of **1** and **2** can gelate several solvents, in particular water, octanol, and diphenyl ether (Table 2). Evidence showing that both gelators are present in the gel fibers was obtained from ^{1}H NMR spectroscopy of a solution of **1** and **2** (2 wt % total, 1:1 molar ratio, in octanol), in which the sharp aromatic proton signals of both **1** and **2** all broadened to the same extent upon

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gelation of the sample.[15] In octanol and dipehenyl ether, an interesting phenomenon was observed: upon heating of a mixture of **1** and **2** in a 1:1 molar ratio, in octanol or diphenyl ether, the two white powders dissolved, yielding a colorless solution that turned into a yellow gel upon cooling to room temperature. Several cycles of heating (gel melting) and cooling (gel formation) of the same sample proved the reversibility of this process and ruled out the possibility of a change in color due to degradation of the gelators. Moreover, ^{1}H NMR spectra of **1** and **2**, after such heating and cooling cycles, also confirmed that the molecular structure of the two gelators had not changed. Interestingly, the single-component gels in the same solvents are colorless. Therefore, the change in color observed for the dual-component system pointed to the occurrence of donor−acceptor interactions between **1** and **2** in the gel fibers.[16,17]

The gelation ability of mixtures of different molar ratios of **1** and **2**, in water, octanol, and diphenyl ether, was studied (Table 2). In the more apolar solvents, a definite change from colorless, or white, to yellow could be observed upon going from the 100:0 or the 0:100 samples to the mixed samples of **1** and **2**. In water, on the other hand, although gelation did occur for mixtures up to a ratio of 60:40 of **1** and **2**, respectively, the samples remained colorless. These results are in agreement with the behavior shown by charge-transfer complexes, whereby solvent polarity plays an important role; in fact, charge-transfer interactions become visible only in nonpolar environments.[16,17,18] In octanol and in diphenyl ether, color intensification was observed for mixed samples containing 50% or more of gelator **2** (Table 2). This phenomenon has previously been observed in solution, by Landauer and McConnell,[17] for samples containing aniline and various nitrobenzenes. Values of the formal extinction coefficients of such samples were found to increase with increasing aniline concentration. The authors attributed this behavior to the existence of 1:1 and 2:1 donor−acceptor complexes, respectively, and thus to light absorption by both of these types of complexes.

To determine whether the donor−acceptor interactions between **1** and **2** induce stabilization of the dual-component gel, T_{gel} measurements with different ratios of the two gelators were carried out.[19] In octanol the T_{gel} of **1** is 93 °C; upon increasing amounts of **2**, the T_{gel} at first decreases before increasing to reach a local maximum (55 °C) at a 1:1 ratio of the two gelators[20] (Figure 1). This behavior is most probably the result of two contrasting effects. Although **1** is a good gelator for octanol, **2** precipitates in octanol; therefore, increasing amounts of **2** in the gel of **1** cause a destabilization of the gel that is reflected in decresing T_{gel} values. However, increasing amounts of **2** also give rise to increased donor−acceptor interactions, which seem to provide stabilization to the dual-component gel system since the T_{gel} values increase to a local maximum. In diphenyl ether, on the other hand, both **1** and **2** form gels and a maximum T_{gel} value was measured for a 1:1 molar ratio mixture of the gelators, showing a stabilization of about 30−40 °C with respect to the gels of the single components (Figure 1). These results indicate that when donor and acceptor moieties are covalently attached to gelators, their interaction can lead to thermal stabilization of the gel, provided that the solvent employed is one which the single components can also gelate.

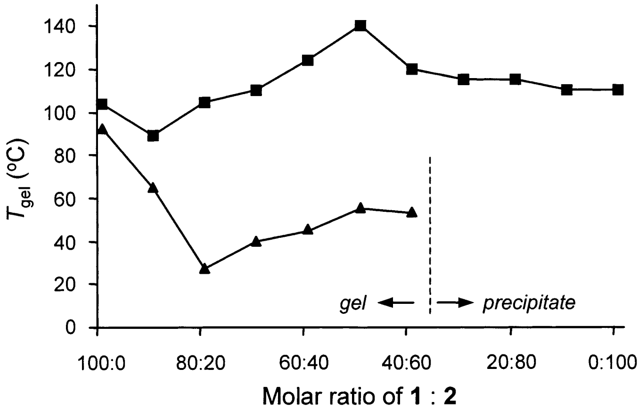

Figure 1. T_{gel} as a function of the molar ratio of **1** to **2**, in dual-component gels in diphenyl ether (■) and in octanol (▲); the dotted line delineates the passage from gel to precipitate for the mixtures in octanol only.

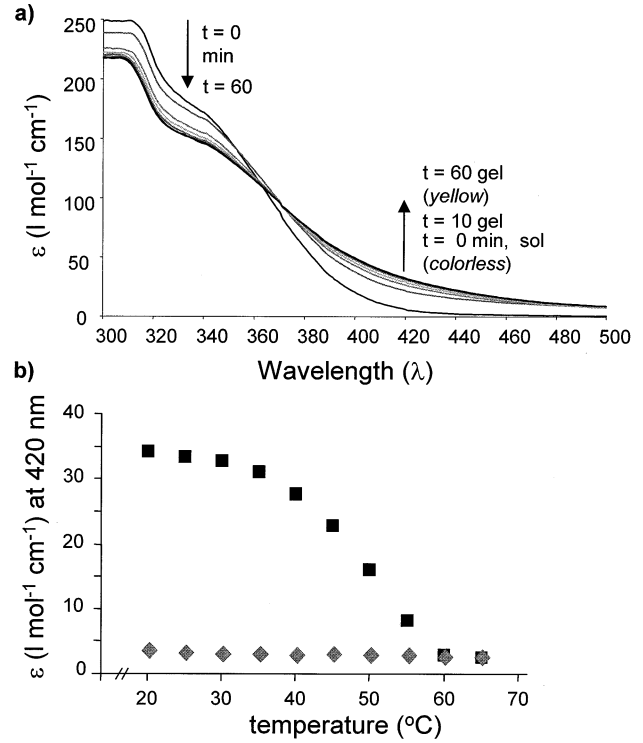

Figure 2. (a) UV−Vis spectra of a 2 wt % sample of **1** and **2**, in a 1:1 molar ratio, in octanol. At $t = 0$ min the sample is completely dissolved, at $t = 10$ min gelation occurs, and between $t = 10$ and $t = 60$ min the yellow color of the gel intensifies considerably, (b) ϵ at 420 nm as a function of the temperature, for a 3 wt % sample (■) and for a 1 wt % solution sample (◆) of **1** and **2**, in a 1:1 molar ratio, in octanol.

To obtain spectroscopic evidence of the donor−acceptor interactions taking place in the dual-component gels, UV−vis spectroscopy was carried out on a sample containing both **1** and **2**, 2 wt % total, in a 1:1 molar ratio, with octanol as the solvent.[21] Under these conditions the sample is initially a solution and slowly becomes a gel within approximately 1 h;

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(15) Before gelation, the peak width at half-height of the aromatic proton signals of **1** at 8.50 and 8.08 ppm and of **2** at 7.54 and 6.94 ppm was 0.025 ppm, while after gelation this value increased to 0.056 ppm for all these signals.

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(19) The T_{gel} was determined by placing an inverted, sealed tube in a thermocontrolled oil bath and increasing the temperature at a rate of 1 °C min^{-1}. Here, T_{gel} is defined at the temperature at which the gel disappears.

(20) For samples containing more than 60% **2**, T_{gel} values could not be determined due to precipitate formation.

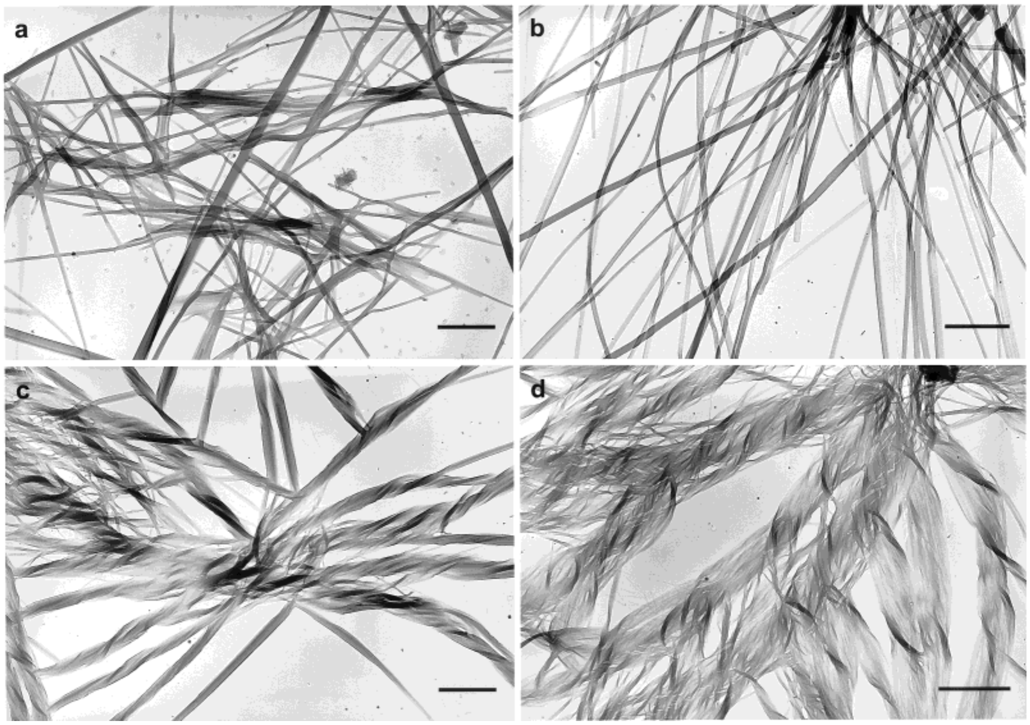

Figure 3. TEM images of a gel of **1** (a), a gel of **2** (b), and a gel of **1** and **2** in a 1:1 molar ratio (c and d), 3 wt %, in diphenyl ether. Scale bars = 1.00 μm.

therefore, the gelation process can be monitored at room temperature (Figure 2a). At first, a decrease in intensity of the shoulder at 335 nm and a simultaneous increase in signal at higher wavelengths (380−800 nm) were observed as the sample changed from sol to gel (from $t = 0$ to $t = 10$ min), becoming only slightly yellow in the process. Subsequently, while the intensity of the shoulder at 335 nm continued to decrease, the intensity of the signal at around 420 nm increased in correspondence to a substantial intensification of the yellow color of the gel. Such light absorption in the 350−600 nm range can be interpreted as intermolecular charge-transfer spectra.[17] These spectra represent electronic transitions between (D, A) and (D^+−A^-), where D is the electron donor (**2**) and A is the electron acceptor (**1**). The reason for intensification of the signal at 420 nm, instead of the appearance of a new shoulder as had previously been observed in solution experiments,[17] is as yet not clear. The charge-transfer band for the complex of **1** and **2** might be broader in the gel than that of the aniline−nitrobenzene complex in solution, due to extensive stacking of the donor and acceptor molecules in the gel fibers. The temperature dependence of the band at 420 nm, for a 3 wt %, 1:1 mixed gel of **1** and **2** in octanol was also examined by UV−vis spectroscopy. The results presented in Figure 2b clearly show that the gelation process is accompanied by a considerable increase in donor−acceptor interaction, while in a true solution of **1** and **2** (1 wt %, 1:1 molar ratio) only a very slight, regular increase of the molar absorption coefficient (ϵ) with decreasing temperature is observed. Furthermore, the effect of the ratio of **1** and **2** on the intensity of the charge-transfer signal in octanol was studied. Interestingly, upon going from a **1**:**2** ratio of 60:40 to 50:50 and then to 40:60, the intensity of the charge-transfer signal (at 420 nm) increases.[22] This observation seems to support the existence of not only 1:1 but also 2:1 donor−acceptor complexes as proposed by Landauer and McConnell (vide supra), explaining the intensification of the UV signal at ratios of **1** and **2** higher than 50:50. However, it should be noted that the T_{gel} values of such mixtures show a maximum for the 50:50 sample (Figure 1). Therefore, although charge-transfer interactions are maximized in samples containing a higher ratio of **2**, maximum thermal stability of the dual-component gel is achieved at a 50:50 ratio of the two gelators.

Transmission electron microscopy images of the dual-component gels in both octanol and diphenyl ether (3 wt %, 1:1 molar ratio) provided further insight into the structure of these organogel systems (Figure 3). In octanol no significant differences were observed between the single-component and the dual-component gels. All consist of networks of relatively straight bundles of fibers approximately 60−200 nm in diameter. In diphenyl ether, however, while TEM images of the single-component gels showed networks of straight fibers (**1**, 30−150 nm; **2**, 20−110 nm in diameter), images of the dual-component gel revealed very large, helical bundles (250−500 nm in diameter) of intertwined fibers (Figure 3c,d). The intertwined fibrous structure of the dual-component gel in contrast to the straight-fiber networks of the single-component gels seem to reflect the increased thermal stability and intermolecular cohesiveness of the former with respect to the latter, as determined by the T_{gel} measurements (vide supra). Small-angle X-ray scattering (SAXS) studies are currently being performed to clarify the structures of the single- and dual-component gels.[23]

Conclusions

In conclusion, we have presented the first example of donor−acceptor interactions in dual-component systems, where both

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[21] Measurements in diphenyl ether were also attempted, but overlap with the diphenyl ether signals did not allow identification of the charge-transfer band.

[22] Lower ratios of **1** and **2** yielded erratic UV signals due to the weak gel formation and to the turbidity of some of the samples, while higher ratios could not be measured due to precipitate formation.

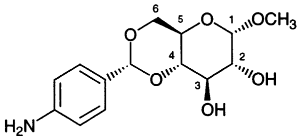
[23] Manuscript in preparation.

donor and acceptor moieties are confined to separate gelators. Furthermore, we have shown how such interactions can bring about effective thermal stabilization of the gel in dependence of the solvent employed and of the donor−acceptor ratio used. Variations on this theme, i.e., different donor and acceptor moieties on a library of sugars, are currently being investigated in the hope of creating materials with novel electronic or optical properties.

Experimental Section

All solvents used were of p.a. grade (Merck). Water was purified by Millipore membrane. ^{1}H NMR spectroscopy was performed on a Bruker ARX 300 apparatus; ^{1}H NMR of a solution and a gel of **1** and **2** (2 wt % in total, 1:1 molar ratio) was measured in octanol with a D_2O probe. UV spectroscopy was performed on a Jasco V-570 UV/vis/NIR spectrophotometer with a 1 mm quartz cell; TEM was performed on a Hitachi H-7100 at 100 kV, and TEM samples were prepared by placing some gel onto a carbon film on a Cu grid and then removing the excess gel after 1 min and allowing the samples to dry overnight at room temperature before imaging. Compound **1** was prepared according to literature procedure.[13]

Methyl 4,6-*O*-(*p*-Aminobenzylidene)-α-D-glucopyranoside (2). Methyl 4,6-*O*-(*p*-nitrobenzylidene-α-D-glucopyranoside (**1**) (570 mg, 1.74 mmol) was dissolved in ethanol (50 mL), 57 mg of palladium on activated carbon (10 wt %) was added, and the suspension was hydrogenated for 30 min. After thin-layer chromatography (TLC) indicated the completion of the reaction, the suspension was filtered and the solvent was evaporated in vacuo. Yield: 505 mg (1.69 mmol) of **2** as colorless solid; 98% of theoretical value.



R$_t$ (ethyl acetate/*n*-hexane 3/1) 0.15; mp 202.7−204.0 °C; ^{1}H NMR (300 MHz, DMSO-d_6) $\delta_H = 3.24-3.41, 3.42-3.63$ (m, 5 H, 3-H, 4-H, 5-H, 6-H), 3.29 (s, 3 H, O*CH*$_3$), 4.08 (dd, $J_{1-H,2-H} = 4.2$ Hz, $J_{2-H,3-H} = 9.3$ Hz, 1 H, 2-H), 4.60 (d, $J = 4.2$ Hz, 1 H, 1-H), 4.96 (d, $J = 6.7$ Hz, 1 H, *OH*), 5.10 (d, $J = 5.2$ Hz, 1 H, *OH*), 5.12 (s, 2 H, *NH*$_2$), 5.33 (s, 1 H, benzylidene-H), 6.49 (d, 2 H, aryl-H), 7.04 (d, 2 H, aryl-H); UV (H_2O, lg ϵ) $\lambda_{max} = 239.4$ nm (3.92); SIMS (glycerol, positive) *m*/*z* 298 (83%, MH^+). Anal. found: C, 56.51; H, 6.53; N, 4.60. Calcd for $C_{14}H_{19}O_6N$: C, 56.54; H, 6.44; N, 4.71.

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