# More than just a catalyst: a novel role for benzylamine in the sol–gel transcription of organogels†

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**Gelator–catalyst interactions allow the transcription of the organogel structure of methyl-4,6-O-(p-nitrobenzylidene)-α-D-glucopyranoside (1) into its silica analogue, even in the absence of positive charges or H-bonding sites on the gelator molecule which, until now, were considered indispensable.**

Inorganic materials can be shaped into a variety of structures using organic, supramolecular assemblies as templates.[1] Vesicles,[2] organic crystals[3] and phospholipid fibers[4] are just some of the organic templates that have successfully been employed to create interesting silica constructs. In addition, we have found that superstructures formed by organogelators act as excellent templates because of their stable, 'solid-like' aggregation behavior. The growth of helical silica is one of the most striking examples of what can be achieved by using organogel fibers as the template for sol–gel polycondensation of tetraethylorthosilicate (TEOS).[5] It has, however, been shown that the presence of some attractive force between the superstructures and TEOS is indispensable for efficent sol–gel transcription. Therefore, up till now, transcription into silica via TEOS polycondensation has been limited to superstructures of molecules that possess a cationic charge in the form of a quaternary ammonium moiety[6] or a metal cation,[5,7] and molecules that possess a H-bonding site in the form of primary amines or combinations of primary and secondary amines.[2,8] The design of new gelators for organogel transcription into silica has, therefore, been strongly limited to molecules containing either positive charges or amino groups.[8] In this paper we show the first example of an organogel that can be successfully transcribed into silica although it does not possess either a positive charge or a H-bonding amino group. We have found that the catalyst for silica formation, i.e. benzylamine, can interact with the molecular aggregates of 1[9] in

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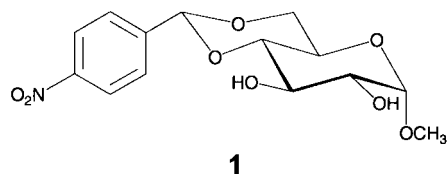
the gel fibers, thus providing the driving force necessary for the transcription process. Clear evidence for the gelator–catalyst interaction has been obtained from transmission electron microscopy (TEM), circular dichroism (CD), ^{1}H NMR and FT-IR spectroscopy measurements.

In water, gelator 1 forms a clear gel consisting of a three-dimensional network of curved fibers[9] (Fig. 1a). An aqueous solution containing 1 (0.5 wt%) and benzylamine (ba) in a 1:1 ratio also yields a clear gel. However, this particular gel consists

of a network of much straighter fibers (Fig. 1b) than those observed for the gel of 1 without benzylamine. The structure of the organogel of 1 is, therefore, altered, to some degree, by the interaction with benzylamine. To transcribe this organic superstructure into silica, polycondensation of TEOS was carried out using an aqueous solution of 1 + ba.[10] After calcination of the sample,[11] TEM images (Fig. 1c and d) showed tubular structures of similar diameter (50–100 nm) and appearance to those observed in the gel samples of 1 + ba, indicating that the transcription was successful. In a sample containing only 1 and TEOS, i.e. no catalyst, no silica formation was observed even after several weeks. Apparently, benzylamine can interact with the molecules of 1 in the gel fibers, most likely via hydrophobic and/or π–π stacking interactions, making transcription of the organogel possible.

To elucidate the gelation process of 1 with benzylamine, experiments were carried out replacing benzylamine with different catalysts: hydrazine and 3,5-dimethoxybenzylamine. Although an aqueous solution of 1 (0.5 wt%) and hydrazine (in a 1:1 ratio) did form a gel, the transcription experiment carried out by adding TEOS to this system yielded only granular silica particles. This result indicates that there is no particular interaction between 1 and hydrazine which can lead to the transcription of the organogel. This observation is in accordance with the assumption that hydrophobic and/or π–π stacking interactions between benzylamine and 1 play a key role in the



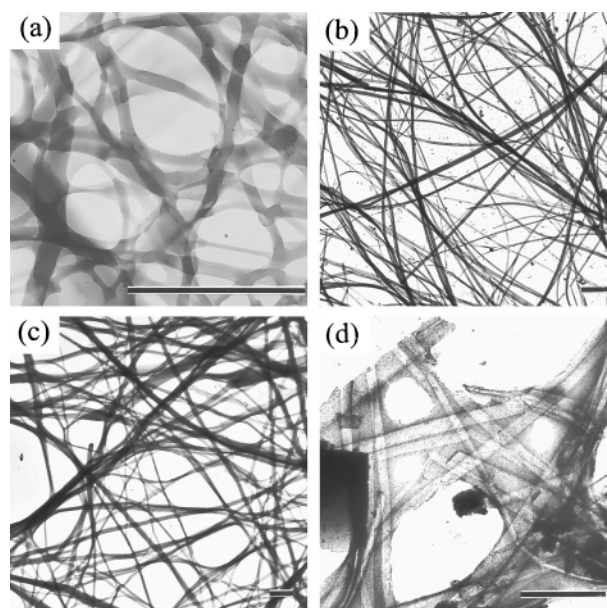**Fig. 1** TEM images of (a) the gel of 1 (scale bar = 0.75 μm), (b) the gel of 1 + ba, (c) the xerogel of 1 + ba + TEOS and (d) the xerogel after calcination (scale bars = 1.50 μm ).

† Electronic supplementary information (ESI) available: CD, FT-IR and temperature dependent ^{1}H NMR spectra. See http://www.rsc.org/suppdata/cc/b1/b108148a/

transcription process. The structure of 3,5-dimethoxybenzyl-amine is similar to that of benzylamine, however, its bulky methoxy substituents should disturb the stacking of **1** and, therefore, prevent organogel formation. Indeed, an aqueous solution of **1** (0.5 wt%) and 3,5-dimethoxybenzylamine (in a 1 : 1 ratio) did not form a gel upon cooling, but a precipitate and, thus, could not be transcribed. These results strongly indicate that benzylamine interacts with **1** *via* aromatic π–π stacking, without considerable disruption of the gel structure. Such interactions bring a number of amino moieties (from the benzylamine) onto the gel fiber surface thereby providing the stimulus for organogel transcription.

CD spectra of a gel of **1** and of a gel of **1** + ba show slight differences which can be attributed to interactions of the catalyst with **1**. The decrease in spectral intensity for the gel of **1** + ba implies that the chiral superstructure originating from the H-bonding interactions among the sugar moieties of **1** is partially destroyed by bound benzylamine molecules. Furthermore, the appearance of a shoulder (215 nm) on the peak at 212 nm suggests the presence of benzylamine in proximity of, or perhaps even intercalated in the gel fibers.

Additional evidence for the interaction of benzylamine with the gel fibers of **1** was obtained from FT-IR measurements (KBr pellet) of the xerogel of **1** and the xerogel of **1** + ba. The spectrum of the xerogel of **1** shows only a rather broad peak (3750–3100 cm$^{-1}$) corresponding to H-bonded OH and NH moieties. However, more signals can be distinguished in the spectrum of **1** + ba, *i.e.* shoulders at 3482 cm$^{-1}$ and 3254 cm$^{-1}$, in comparison with the spectrum of the xerogel of **1** alone. These signals most likely arise from the partial disruption of the H-bonding network of the OH groups in the gel fibers by the interaction of the amino moieties of the catalyst with the gelator molecules within or between the fibers.

To obtain a more detailed picture of the gel of **1** + ba in water, temperature-dependent $^1$H NMR spectroscopy was performed. The peaks of the gelator and of the benzylamine appear broadened in the spectrum of the gel at 298 K. This line-broadening effect for the gelator molecules is typical of organogel samples due to the restricted molecular motion in the gel state with respect to the solution state.[12] Moreover, broadening of the benzylamine peak can be attributed to a decreased mobility of some of the benzylamine molecules, deriving from their intercalation in the gel fibers of **1**.[13] However, the integrals for the peaks of the benzylamine and the gelator protons show a 1 : 1 ratio of both components only in the solution state (343 K), while in the gel state (298 K) the amount of benzylamine appears to be approximately 3 times larger than the amount of **1**. This shows that in the gel, the benzylamine molecules are, on average, more mobile than the molecules of **1** and, therefore, only some are incorporated in the gel fibers, while most are probably situated between the fibers. To determine the actual amount of benzylamine trapped in the gel fibers of **1**, xerogels of **1** + ba were prepared by freeze drying the aqueous samples for 8, 14, 18, 24 and 36 h. The samples were then dissolved in CD$_2$Cl$_2$ and the ratio of benzylamine to gelator was determined by measuring the integrals of the corresponding aromatic proton peaks in the NMR spectra. The amount of benzylamine in the samples decreased with freeze drying time, to reach a steady value of 10–20% after approximately 14 h (Fig. 2). No further decrease was observed even after freeze drying for 36 h. As a reference, a sample containing only benzylamine and water, but no gelator, was subjected to the same treatment and after 24 h no benzylamine could be detected by NMR spectroscopy. Therefore, the amount of benzylamine intercalated/trapped in the gel fibers of **1** seems to be approximately 10–20% of the total number of gelator molecules. These results are in agreement with the temperature-dependence NMR experiments, which showed only a partial
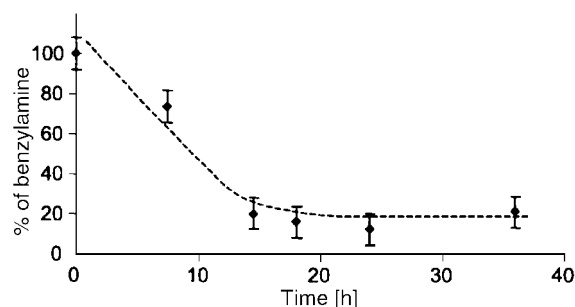


**Fig. 2** Percentage of benzylamine in samples of **1** + ba as a function of freeze drying time (---- line to guide the eye).

broadening of the signals of the benzylamine protons in the gel state, as well as an increase in the integral ratio of benzylamine to gelator.

In conclusion, we have shown that the organogel of a compound which does not contain a positive charge or an amino group can still be transcribed into a silica structure, as long as the catalyst for the polycondensation process can interact with the gelator molecules. Preliminary results using other gelators that do not contain positive charges or amino groups either,[14] indicate that this phenomenon is of a general nature. As a consequence, the transcription of a much broader range of organic superstructures, such as proteins, neutral vesicular aggregates or polysaccharides, *via* the polycondensation of TEOS can now be taken into consideration. Being able to transcribe such entities will undoubtedly lead to a greater variety of inorganic materials with interesting new shapes and properties.

## Notes and references

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