A tailored organometallic gelator with enhanced amphiphilic character and structural diversity of gelation†

Thorsten Klawonn, Andreas Gansäuer, Iris Winkler, Thorsten Lauterbach, Dieter Franke, Roeland J. M. Nolte, Martin C. Feiters, Hans Börner, Jens Hentschel and Karl Heinz Dötz

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A cholesterol-appended titanocene gelator was synthesised which forms twisted fibers able to gelate a variety of solvents of different polarity as demonstrated by spectroscopic and microscopic techniques.

The development of novel structures and materials based on the gelation of solvents by low molecular mass gelators (LMGs) is a rapidly expanding area of interdisciplinary research. However, a rational structural design of LMGs still remains a major challenge.1–5 A promising approach is based on the concept of ALS gelators.2,4–7 These compounds consist of an aromatic unit (A) connected via a linker (L) to a stoichiometric entity (S), typically cholesterol. So far, only a very limited number of ALS gelators have emerged that are able to gelate a variety of solvents of different polarity.7

Here, we report our preliminary results on a novel amphiphilic organometallic ALS gelator based on a metallocene. It is known that incorporation of an apolar ferrocene or even the charged ferrocenium moiety into ALS type molecules does not result in gelation as documented for a number of solvents.8 Our approach is based on the replacement of the apolar aromatic system by a polar titanocene unit that is able to strongly interact through its Lewis-acidic site with polar solvents which may result in the gelation of these solvents as well as in unusual structural motifs in the final gel. This may lead to an improvement with respect to previous work published in the literature.2,4–8 Three cholesterol containing titanocenes shown in Fig. 1 have been synthesised by the recently established modular route.9 It turned out that the substitution pattern around the titanocene unit is crucial for the gelation abilities of the complexes. Complex 1 containing the cyclopentadienyl ligand and the geminal methyl groups represents an excellent gelator for a variety of customary solvents as summarized in Table 1; in fact, it acts as a "supergelator"9 with a critical gelation concentration of < 1 wt% for toluene, benzene, ethyl acetate and acetone. Complex 1 represents a second rare example of organometallic low molecular mass gelators.11

The cyclohexyldiene derivative 2 requires distinctly higher concentrations for gelation to take place, which, however, are too high to be of practical use. Permethylation of the terminal cyclopentadienyl ring as in 3 results in a complete loss of the gelating ability which clearly indicates the role of the titanocene moiety in the gelation process. This conclusion is strongly supported by the analysis of temperature-dependent 1H-NMR spectra of the gels of 1. In C6D6 at room temperature the experiments display strongly broadened signals of the cholesterol moiety and slightly less broadened resonance absorptions for the titanocene moiety as concluded from a comparison with the UV–Vis spectra of Cp2TiCl4. Upon warming, the 

Table 1 Gelation ability of 1 (further solvents and details are given in ESI)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>cgg [wt%]</th>
<th>Tgel [°C]</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6H6</td>
<td>0.6</td>
<td>53–56</td>
<td>transparent</td>
</tr>
<tr>
<td>CH2Cl2</td>
<td>4.0</td>
<td>10–10</td>
<td>transparent</td>
</tr>
<tr>
<td>CH2COCH3</td>
<td>0.8</td>
<td>40–44</td>
<td>turbid</td>
</tr>
<tr>
<td>CH2SOCH3</td>
<td>1.5</td>
<td>53–58</td>
<td>turbid</td>
</tr>
</tbody>
</table>

† Electronic supplementary information (ESI) available: Sample preparations, CD-, TEM-, cryo-SEM-equipment, temperature dependent NMR, further EM-images. See DOI: 10.1039/b701565h

Fig. 1 Steroid-modified titanocene complexes studied for gelation abilities (see ESI for details).

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the CD-effect decreases thermoreversibly,\textsuperscript{13} until the sol is CD-silent at 85°C. The results obtained from both spectroscopic techniques consistently reveal the occurrence of self-assembly and supramolecular chirality within the gel induced by the chiral centers present in the steroid part.

Transmission electron microscopy (TEM) images of dried gels of 1 in toluene and acetone (Fig. 2, upper panels) reveal that for both solvents a fibrous network, typical for gels of low molecular mass gelators, is formed. However, the networks differed significantly in their dimensions: in toluene, long twisted architectures with a diameter of 65–105 nm consisting of intertwined fibers (15–35 nm) are generated that aggregate to form helices fringing out at the end. In contrast, in acetone, the twists are considerably shorter (6–10 μm) but noticeably thicker (600–900 nm).

Cryo-scanning electron microscopy (cryo-SEM, Fig. 2 lower panels) was applied as a direct mild method to examine the 3D gel structure in the presence of the frozen solvent. Thus, the effects of drying of the wet gels necessary for TEM could be investigated. The overall appearances of the TEM and cryo-SEM pictures were quite similar which demonstrates that the drying process does not affect significantly the gel network.

AFM images of dried samples of 1 obtained from toluene unambiguously revealed the helicity of the three-dimensional network with intertwining and fringing of the fibers. Mostly, the twists were left-handed (M); nevertheless some right-handed strands (P) are also apparent. Both helical forms are depicted in Fig. 3. The concomitant occurrence of both left- and right-handed helices is a common feature of ALS gelators and, for example, has also been observed for anthracene- and azobenzene-derived gelators.\textsuperscript{6,7} In summary, our results demonstrate that an also been observed for anthracene- and azobenzene-derived helices is a common feature of ALS gelators and, for example, has significant for the interactions with the solvent. The elementary fibers further intertwine to generate hierarchically defined structures as documented by the microscopic techniques.

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Notes and references

\textsuperscript{†} Experimental data, sample preparation, further EM-images, CD-, TEM-, cryo-SEM-, AFM-equipment and methods are given in ESI.


