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A Tailored Organometallic Gelator with Enhanced Amphiphilic Character and Structural Diversity of Gelation

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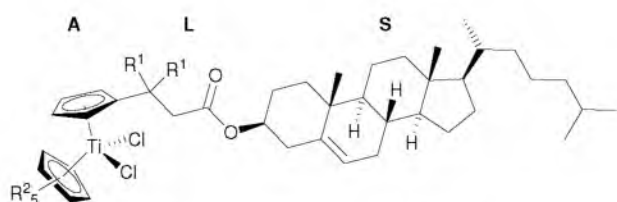
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A cholesterol-appended titanocene gelator was synthesised which forms twisted fibers able to gelate a variety of solvents of different polarity as demonstrated by spectroscopic and microscopic techniques.

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 steroidal 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 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



1: R¹ = CH₃, R² = H; **2:** R¹, R¹ = (CH₂)₅, R² = H; **3:** R¹ = CH₃, R² = CH₃.

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

excellent gelator for a variety of customary solvents as summarized in Table 1; in fact, it acts as a “supergelator”⁷ with a critical gelation concentration of < 1 wt % for toluene, benzene, ethyl acetate and acetone. Complex **1** represents the second rare example of organometallic low molecular mass gelators.¹¹

The cyclohexylidene 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 cyclopentadienyl ligands (see ESI). All these signals sharpen significantly with increasing temperature indicating a partial deaggregation. This temperature dependence is reversible; upon cooling the initial spectra are observed again. The cholesterol moiety is able to induce “supramolecular chirality”¹² in the process of gelation as demonstrated by the CD-spectra of **1** (1.5 wt% in di-*n*-butyl ether) in the gel state (see ESI). A distinct CD-effect is observed with an exciton coupling intersecting the x-axis at a maximum absorption of λ_{max} = 249 nm which can be assigned to the π-π* transition in the titanocene moiety as concluded from a

†Electronic Supplementary Information (ESI) available: sample preparations, CD-, TEM-, Cryo-SEM-equipment, temperature dependent NMR, further EM-images. See <http://dx.doi.org/10.1039/b000000x/>

Table 1 Gelation ability of **1** (further solvents & details are given in ESI).

solvent	cgc ^a [wt%]	T _{gel} ^b [°C] 1.5 wt%	appearance
C ₆ H ₆	0.6	53-56	transparent
CH ₂ Cl ₂	4.0	-10 ^c	transparent
CH ₃ COCH ₃	0.8	40-44	turbid
CH ₃ SOCH ₃	1.5	53-58	turbid

^a critical gelation conc., ^b gel-sol transition temperature^{10,11}, ^c 4 wt%.

comparison with the UV/Vis spectra of Cp_2TiCl_2 . Upon warming, the CD-effect decreases thermoreversibly¹³ 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 centres 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

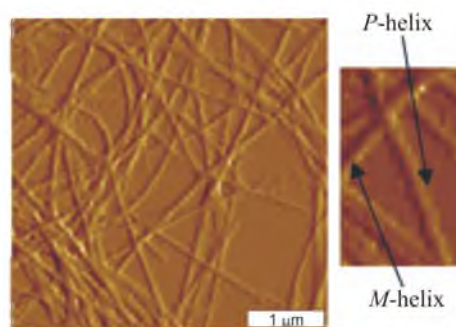


Fig. 3 AFM-image of **1** in toluene (1.5 wt%).

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 3 D gel

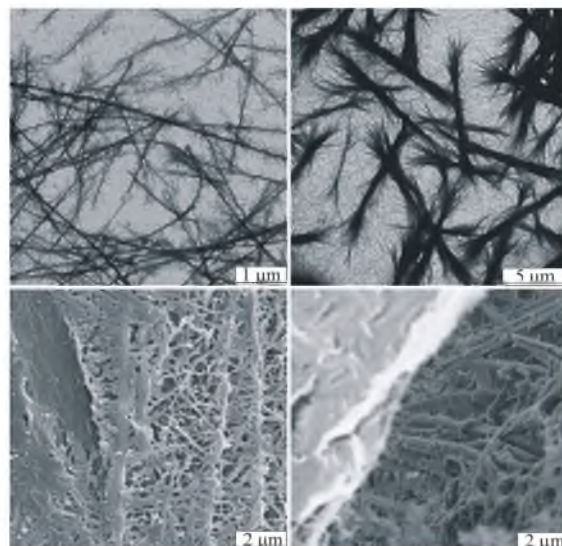


Fig. 2 TEM (upper panels) and cryo-SEM (lower panels) images of **1** (1.5 wt%) in toluene (left) and acetone (right).

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 appearance 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.^{6,7} In summary, our results demonstrate that an organometallic functionality such as the titanocene unit in **1** can substitute the classical arene moiety in ALS gelators. The structural data for **1** are compatible with the aggregation model proposed for ALS gelators by Weiss⁶ and Shinkai⁷. Thus, we suggest a similar stacking model for the cholesterol moieties through van der Waals interactions responsible for the formation of the archetypal spiral staircase.

As a consequence, the titanocene units are shifted towards the periphery of the helix and, thus, may be responsible for the interactions with the solvent. The elementary fibers further intertwine to generate defined hierarchically structures as documented by the microscopic techniques.

Notes and references

† Experimental data, sample preparation, further EM-mages, CD-, TEM-, Cryo-SEM-, AFM-equipment and methods are given in ESI.

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