Modular construction and hierarchical gelation of organooxotin nanoclusters derived from simple building blocks†‡

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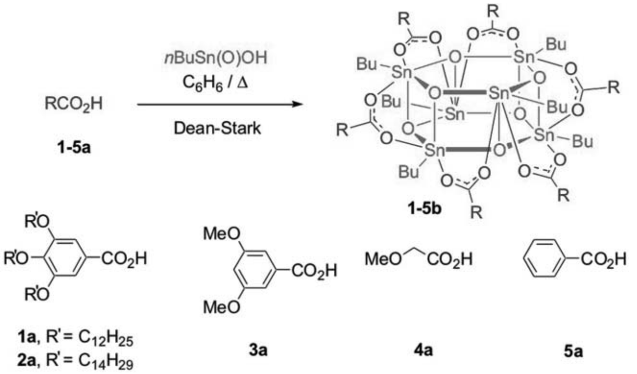
Mixtures of an appropriate carboxylic acid and *n*-butylstannoic acid constitute modular gelation systems, in which the formation of a well-defined 'tin-drum' nanocluster subsequently underpins the hierarchical assembly of nanostructured fibres, which form self-supporting gel-phase networks in organic solvents.

Understanding the controlled self-assembly of nanoscale architectures from simple well-defined molecular-scale building blocks provides a major challenge to chemical science and a source of nanostructured advanced materials.[1] Over recent years, a wide range of structurally diverse, low molecular weight gelators has been developed.[2] These molecules assemble through non-covalent interactions into nanoscale fibres, which ultimately form sample-spanning interpenetrated networks. These networks, although only constituting a small percentage (*e.g.* 1% wt/vol) of the total sample, are capable of preventing the flow of bulk solvent, through a combination of capillary forces and solvent–gelator interactions. In these materials, molecular scale information programmed by organic synthesis is expressed on the macroscopic level *via* nanoscale self-assembly. This approach generates soft materials with diverse applications.[3] Modular[4] and multi-component[5] gelation systems have been of specific interest as they have exquisite tunability and there is great potential to introduce function. Modular systems rely on the development of molecular scaffolds which act as generic gelating units. Examples of multi-component systems include complexes formed through acid–base interactions[6] or metal–ligand bonds[7] which subsequently assemble into fibres *via* other non-covalent interactions. This paper reports our preliminary characterisation of a novel and unexpected modular, multi-component gelation system, in which tin assembles with carboxylate ligands to yield organooxotin nanocluster modules, which then hierarchically assemble into gels.



Scheme 1 Gelators investigated in this paper.

The formation of organooxotin clusters has been of considerable interest owing to the structurally diverse products which can be generated in a simple one-pot assembly process (Scheme 1).[8] For example, ferrocenes,[9] porphyrins[10] and fullerenes[11] have all been assembled around the 'tin-drum' nanocore. The clusters in this paper were synthesised by heating the appropriate carboxylic acid and *n*-butylstannoic acid in benzene under Dean–Stark conditions (Scheme 1) and fully characterised (see ESI†). Intriguingly, during the synthesis, gelation of some samples occurred. Although the supramolecular packing of tin-drums in crystals has previously been explored,[12] there have been no previous reports of tin-drum gelators, and we therefore became interested in the behaviour of these nanoclusters.

We investigated the gelation of **1b** in benzene, using simple, reproducible tube-inversion methodology to monitor the temperature of the gel–sol phase boundary (T_{gel}) at a range of concentrations (Fig. 1).[13] As commonly observed, increasing the concentration of the gelator increased the T_{gel} value until a plateau value was reached. Gelator **1b** forms room temperature gels at concentrations of *ca.* 5 mM (2.6 wt%), and the T_{gel} value then increases to its plateau value of 57.5 °C at a concentration of

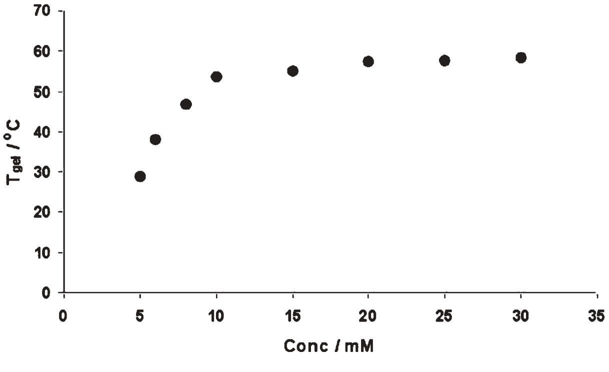


Fig. 1 T_{gel} data as a function of concentration (in benzene) for gelator **1b**.

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† Electronic supplementary information (ESI) available: Synthesis and characterisation data. See DOI: 10.1039/b710971g

‡ The HTML version of this article has been enhanced with a colour image.

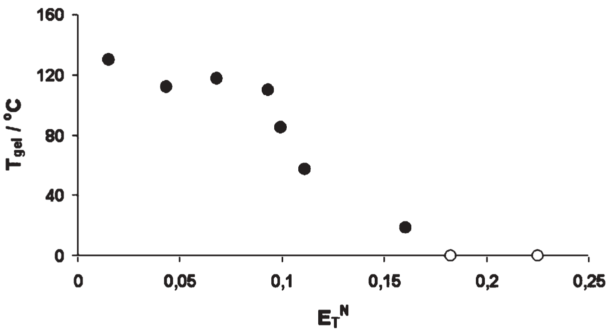

Fig. 2 T_{gel} data determined in different solvents plotted as a function of the normalised Reichardt solvent parameter – open circles indicate that gelation was not observed.

10 mM (5.2 wt%). The increase in the macroscopic thermal stability of the system on increasing concentration corresponds to the evolution of a sample-spanning network. In the 'plateau region', addition of further gelator no longer enhances the materials properties, suggesting that the network has achieved its optimal structure in terms of fibre growth and the number of network contact points.

We considered the possibility that the gelation process may represent a chemical change in the tin-drum nanocluster. However, in all cases, gelation was thermoreversible. Furthermore, there was no difference in the NMR spectra (^{1}H, ^{13}C and ^{119}Sn) before and after gelation, demonstrating that the gelation of these nanoclusters is a physical process based on non-covalent interactions between clusters and does not correspond to a chemical transformation.

We next investigated the influence of solvent on the gelation of **1b** in order to gain further insight into the self-assembly mechanism.[14] The thermal properties of **1b** were determined at constant concentration (20 mM) in a range of different solvents. The T_{gel} values could be related to the solvent polarity parameter E_T^N (Reichardt's polarity parameter) (Fig. 2).[15] In general terms, T_{gel} decreased as E_T^N increased,§ and if the solvent became too polar, then gelation was no longer observed. This indicates that the non-covalent interactions between the clusters which underpin gelation have an electrostatic component (*e.g.* dipole–dipole interactions between Sn($\delta+$) and O($\delta-$)).

We then carried out a thermal investigation of all of these new gels (Table 1), determining the concentration and weight % required for the onset of network 'saturation', as well as the T_{gel} value in the plateau region. Modifying the peripheral groups of the organooxotin nanoclusters directly controls the concentration at which the plateau region is established. Nanoclusters **1b** and **2b**, with peripheral aliphatic tails, are the most potent gelators, reaching saturation at low concentrations (*ca.* 10 mM). Gelators **3b** and **4b** are less effective, requiring concentrations of 30 mM and 100 mM respectively to achieve saturation. In terms of the number of molecules required for gelation, nanoclusters **1b** and **2b** are therefore most effective – indicating that they have higher self-assembly association constants. Furthermore, although **1b** and **2b** have higher molecular masses (M_r) than **3b** and **4b**, they are also more effective in terms of weight % loading. This indicates that alkyl tails enhance the assembly process, possibly through van der Waals interactions.

Table 1 Summary of thermal characterisation of gelators **1**–**5** in benzene

Code	M_r	Onset of plateau region/mM	Onset of plateau region/wt%	Plateau region T_{gel}/°C
1b	5195.3	10	5.2	57.5
2b	5700.3	10	5.7	59.5
3b	2237.8	30	6.7	62.5
4b	1589.2	100	15.9	53.5
5b[a]	1877.5	50	9.4	50

[a] Solvent: 1-bromonaphthalene.

Gelators **1b**, **2b** and **3b**, which contain aromatic rings, are all significantly more effective than gelator **4b**. In this case, the aromatic rings are replaced with methyl ether groups indicating that π–π stacking, as previously observed in tin-drum crystals,[12] may play an important role in the assembly process.

Interestingly, although nanoclusters **1b** and **2b** are the most potent gelators at low concentration, once the plateau region is attained the macroscopic thermal stability is relatively independent of the peripheral groups, with the T_{gel} values of all gelators being between 50 °C and 65 °C. This indicates that although **1b** and **2b** have higher affinities for self association, their 'plateau-region' network formation is somehow limited (see below).

Nanocluster **5b** only formed gels in 1-bromonaphthalene – in other solvents either dissolution or precipitation occurred. In 1-bromonaphthalene, a cloudy gel with a plateau region T_{gel} value of 50 °C was observed – effective gelation given that this solvent is more polar than toluene.¶ Interestingly, **5b** is the only nanocluster in which the aromatic ring is not substituted by ethers. We propose that the absence of ethers modifies the solubility properties of **5b**, highlighting the fact that gelation is a delicate balance between solvation, self-assembly and precipitation events.[16]

Field emission gun scanning electron microscopy (FEGSEM) of the xerogel of **1b** (Fig. 3, dried from benzene) indicated the formation of 'one-dimensional' interpenetrated nanofibres *ca.* 50 nm in width. Surprisingly, however, these fibres were relatively short, typically having lengths of only *ca.* 400 nm. Usually, the fibres underpinning gels are many micrometres long.[2] It has been reported that steric hindrance on the periphery of fibrillar architectures can limit the lengths to which they grow;[17] we propose that the alkyl chains on the periphery of nanocluster **1b** may limit fibre growth and hence explain why the T_{gel} of nanocluster **1b** was limited in the plateau regime. Unfortunately all other gels proved difficult to image reproducibly from benzene.

Wide-angle X-ray powder diffraction (XRD) can help elucidate the molecular structure of organogels.[18] We therefore performed a preliminary investigation of the xerogel of **1b** (dried from benzene), and the XRD pattern (Fig. 4A) revealed a series of sharp peaks,

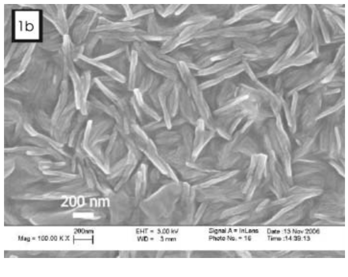

Fig. 3 FEGSEM image of gelator **1b** as a benzene xerogel.

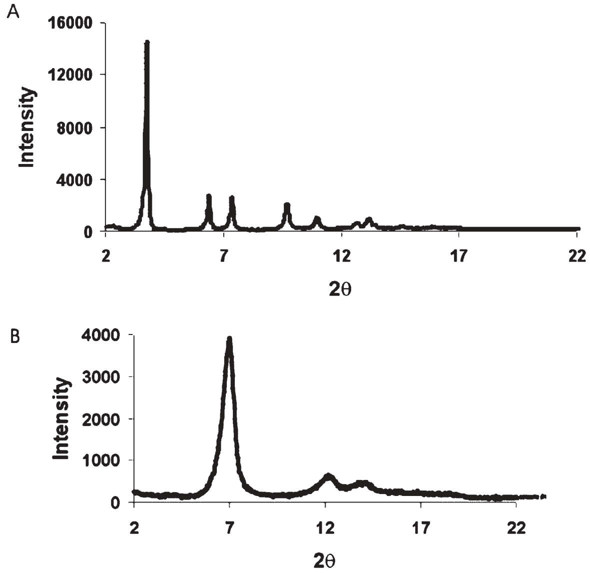

Fig. 4 XRD patterns of the xerogels (from benzene) formed from (A) gelator **1b** and (B) gelator **3b**.

indicative of ordered structures. The first three peaks could be indexed as hexagonal packing (23.47 Å, 13.83 Å, 11.99 Å, representing spacings of 1, $1/\sqrt{3}$, $1/\sqrt{4}$, respectively). Only the major peaks could be indexed – the minor peaks may represent different structuring, or a degree of polymorphism, in the powder. Gelator **3b** had broader diffraction peaks, which indicates that in the absence of alkyl tails the packing is less ordered, reinforcing the importance of these groups in generating an ordered assembly. Again, the peaks could be preliminarily indexed to hexagonal packing (12.60 Å, 7.23 Å, 6.30 Å), the smaller dimensions being consistent with smaller nanoclusters (*i.e.* no alkyl tails). More detailed X-ray studies will be a focus of future work on this system.

Crystallography[10,12] indicates that tin-drum nanoclusters are flattened cylinders with the carboxylic acid ligands arranged around the equator. Disc-like objects are an appropriate shape for self-assembly (stacking) into columnar structures.[12,19] Indeed, a single crystal X-ray structure of compound **5b** (to be reported elsewhere), which is similar to **3b**, indicated a cluster diameter of 19.7 Å and height of 14.5 Å. Due to interdigitation, the cluster–cluster repeat length was *ca.* 13 Å. Our results are consistent with a model in which the nanoclusters assemble into hexagonally packed columnar fibrils. We propose that columnar aggregation is driven by electrostatic interactions, for example between Sn(δ+) and O($\delta-$), combined with π–π stacking interactions for **1–3b**. Furthermore, van der Waals interactions and the packing of alkyl chains support assembly for **1–2b**.

In conclusion, this preliminary communication reports a novel multi-component gelation system based on the assembly of 'tin-drum' modules which hierarchically assemble into fibrillar nanomaterials. The clusters form as a consequence of tin–carboxylate (metal–ligand) interactions, and then hierarchically assemble into fibres as a consequence of polar interactions (dipole–dipole interactions and π–π stacking) supported by van der Waals forces. The nanocluster module is highly tunable – a wide range of different carboxylic acids may be employed to assemble structures of this type. Further work is currently in progress to explore the assembly of nanostructures incorporating different carboxylic acids. This will yield greater control over self-assembly, tune the materials properties of the gels, and yield highly functional hierarchical hybrid nanomaterials.

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Notes and references

§ In previous hydrogen-bond mediated gels we have observed dependence on the Hildebrand polar solubility parameter;[14a] however, in this case, no correlation was observed.

¶ Although the normalised Reichardt parameter for 1-bromonaphthalene is not provided in reference 15, those of 1-chloronaphthalene and 1-iodonaphthalene are 0.194 and 0.191 respectively.

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