CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200801475

Self-Assembly of Two-Component Gels: Stoichiometric Control and Component Selection

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Abstract: Two-component systems capable of self-assembling into soft gel-phase materials are of considerable interest due to their tunability and versatility. This paper investigates two-component gels based on a combination of a L-lysine-based dendron and a rigid diamine spacer (1,4-diaminobenzene or 1,4-diaminocyclohexane). The networked gelator was investigated using thermal measurements, circular dichroism, NMR spectroscopy and small angle neutron scattering (SANS) giving insight into the macroscopic properties, nanostructure and molecular-scale organisation. Surprisingly, all of these techniques confirmed that irrespective of the molar ratio of the components employed, the "solid-like" gel network always consisted of a 1:1 mixture of dendron/diamine. Additionally, the gel network was able to tolerate a significant excess of diamine in the "liquid-like" phase before being disrupted. In the light of this observation, we investigated the ability of the gel network structure to evolve from mixtures of different aromatic diamines present in excess. We found that these two-component gels assembled in a component-selective manner, with the dendron preferentially recognising 1,4-diaminobenzene (>70%), when similar competitor diamines (1,2- and 1,3-diaminobenzene) are present. Furthermore, NMR relaxation measurements demonstrated that the gel based on 1,4-diaminobenzene was better able to form a selective ternary complex with pyrene than the gel based on 1,4-diaminocyclohexane, indicative of controlled and selective π–π interactions within a three-component assembly. As such, the results in this paper demonstrate how component selection processes in two-component gel systems can control hierarchical self-assembly.

Keywords: dendrimers • gels • self-assembly • soft materials

Introduction

Self-assembled organic nanostructures[1] are at the forefront of chemical nanoscience as a consequence of their aesthetically appealing architectures, academic challenge, and potential applications in diverse fields including regenerative medicine, biomineralisation, materials synthesis and electronic device construction.[2] Intense research efforts are being devoted towards the design, investigation and understanding of molecular gels.[3] In these materials, low-molecular-weight building blocks assemble in solution through self-complementary non-covalent interactions to yield nanoscale assemblies, which form a sample spanning network and hence exhibit macroscopic gel-phase materials behaviour. Gelation systems which rely on the presence of two complementary components have an additional level of control in the hierarchical assembly process—initially the two components must form a complex, and only then can further assembly into nanoscale architectures take place.[4] A wide range of two-component systems based on different non-covalent interactions has been reported.[5–8] The two-component approach endows gel-phase materials with exquisite microstructural tunability, as either of the two components can be subtly modified. Furthermore, it is possible to tune the network structure by altering the molar ratio of the two components. For example, we reported systems in which varying the molar ratio of the two components could induce dramatic morphological changes,[9] while Lee and co-work-

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ers also recently reported a two-component gel in which the thermal and morphological properties were also modified and under certain conditions microtubule formation was even observed.[10]

Gel-phase materials can readily incorporate functionality, switchability and guest responsiveness. For example, Shinkai and co-workers developed a gel capable of colorimetric detection, able to differentiate between different classes of electron-rich aromatic compounds (i.e., detecting dihydroxynaphthalenes rather than alkoxy- and hydroxynaphthalenes).[11] Naked-eye differentiation of different dihydroxynaphthalene isomers was achieved based on a macroscopic colour change of the gel. Steed and co-workers reported an elegant example in which gelation was triggered in response to the presence of fluoride anions.[12] In addition, we used crown ethers to incorporate cation responsiveness,[13] and a range of other gels with sensory properties have also been reported.[14]

Previously, we have investigated the basic design principles of a dendritic two-component gelator system.[15] This system utilised the interaction between an aliphatic diamine and dendritic building blocks based on L-lysine repeat units. The two components form a complex as a consequence of acid–base hydrogen-bond interactions (with possible associated proton transfer). Intermolecular hydrogen bonding between peptide groups on neighbouring complexes then drives fibre formation, which ultimately underpins network formation and macroscopic gelation. Our detailed studies have highlighted the roles of the spacer chain length,[16] dendritic generation,[17] solvent,[18] stereochemistry,[19] molar ratio,[9] hydrogen-bonding units,[20] and solubility[21] in controlling self-assembly. We recently became interested in using different, more rigid diamines, such as 1,4-diaminobenzene, and in the process of our investigations we uncovered clear stoichiometric control of the self-assembly process as reported in this paper. The "solid-like" networked gelator always had the same stoichiometric composition, and intriguingly, it could tolerate the presence of excess diamine in the "liquid-like" solvent phase. This opened the possibility of exploring self-assembly from mixtures of excess diamine, and we report here that component-selective self-assembly (self-sorting) was observed. Component-selective self-assembly (self-sorting) from complex mixtures of building blocks is an important area of contemporary chemical research.[22] We have previously reported the ability of multicomponent gelators to self-organise into different nanoscale networks,[23] however the approach outlined in this paper, for the first time allows us to quantify the extent to which molecular scale information controls the selective self-assembly process.

Results and Discussion

Characterisation of two-component gelation system: As a first stage in our exploration of rigid diamines, we initially screened the ability of structurally diverse aromatic diamines to form gel-phase materials in toluene in the presence of the second component, generation two L-lysine-based dendron, **G2-COOH** (Figure 1).[24] Most aromatic diamines, such as 1,5-diaminonaphthalene, 1,8-diaminonaphthalene, 3,4-diaminodiphenylmethane and 9,10-diaminophenanthrene remained insoluble in toluene, even in the presence of the dendron. In fact, gels could only be formed from a limited range of rigid diamines, primarily 1,4-diaminobenzene (**1,4-BZ**) and *trans*-1,4-diaminocyclohexane (**1,4-CH**). Additionally, systems based on 1,3-diaminobenzene formed irreproducible partial gels, but the 1,2-diaminobenzene analogue did not form gels under any conditions. This highlights the importance of ensuring the correct relative positions of amine groups on the rigid spacer unit for gel formation to be observed. It may also reflect the enhanced basicity of **1,4-BZ** compared to the positional isomers, with $pK_a(1)$ of the conjugate acid of **1,4-BZ** being 6.08, compared with 4.88 and 4.47 for **1,3-BZ** and **1,2-BZ** respectively.[25]

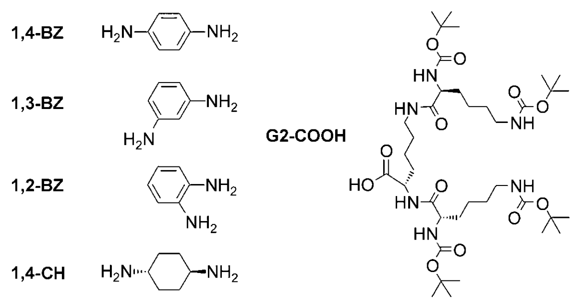

Figure 1. Structure of dendron (**G2-COOH**) and rigid spacer units used for the construction of gels.

From the results of our previous research using flexible spacer units, it was clear that the dendron/diamine molar ratio could directly control network formation and structure, with optimum bundles of fibres having been formed at a 2:1 dendron/diamine molar ratio.[9] On the addition of further diamine, the gel network evolved and its macroscopic thermal stability decreased, until ultimately nanosized flattened platelet-like aggregates were observed at a 1:4.5 stoichiometry. We therefore decided to elucidate the effect of molar ratio on gelation using rigid diamines, **1,4-BZ** and **1,4-CH**. The macroscopic behaviour of the gel was initially determined by monitoring the transition from an immobile to a mobile self-assembled state using tube-inversion experiments across a range of molar ratios (stoichiometries). This simple, reproducible methodology is widely used for preliminary investigations of low molecular weight gelators.[26] Unexpectedly, for both gelators, the anticipated 2:1 dendron/diamine ratio did not form gels, instead resulting in optically transparent solutions. On the other hand, in both cases, increasing the amount of diamine to provide a 1:1 dendron/diamine molar ratio led to macroscopic gelation, with T_{gel} values $\approx 42\,^{\circ}C$.

Figure 2 illustrates the effect on thermal stability of changing the dendron/diamine molar ratio. Notably, on in-

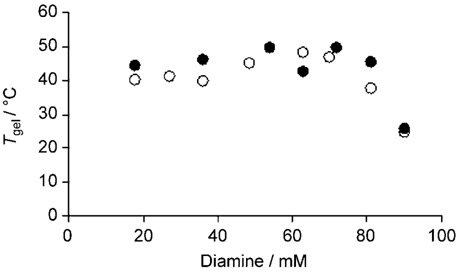

Figure 2. Effect of molar ratio (dendron/diamine) on the gel–sol transition temperature (T_{gel}). For each measurement [dendron] = 18 mM and solvent = toluene; ○ = 1,4-diaminocyclohexane, ● = 1,4-diaminobenzene.

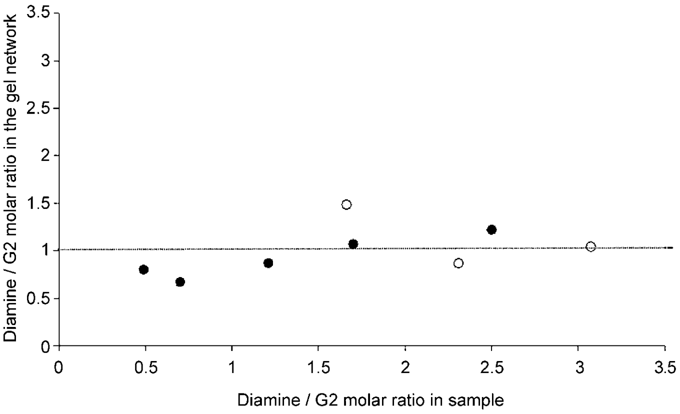

Figure 3. Plot of diamine/dendron molar ratio present in the "solid-like" network (as measured by ^{1}H NMR using diphenylmethane as internal standard) against the molar ratio present in the overall sample. Solvent = toluene, ○ = 1,4-diaminocyclohexane, ● = 1,4-diaminobenzene.

creasing the diamine content beyond the 1:1 molar ratio (i.e., above 18 mM), the T_{gel} values for both systems were surprisingly independent of the molar ratio, suggesting that the network structure that optimally underpinned macroscopic gelation at a 1:1 ratio was unaffected by the presence of increasing amounts of diamine. However, increasing the amount of diamine even further, beyond ≈1:4 dendron/diamine molar ratio, resulted in an incremental decrease in the thermal stability of the material. The gels based on **1,4-BZ** and **1,4-CH** spacer units both exhibited similar thermal behaviours and 1:1 stoichiometric molar ratios for gelation.

It is worth noting that previous work by McPherson and co-workers has shown that structural differences in the spacer unit can influence the molar ratio at which gelation occurs.[5e,27] For example, the optimal molar ratio for gel formation based on bis(2-ethylhexyl) sodium sulfosuccinate (AOT) and 4-nitrophenol was 1:1, whereas for the system based on AOT/2,6-dihydroxynaphthalene, gel formation occurred at a ratio of 50:1.

Based on our unexpected observations, we became interested in elucidating the true stoichiometry of the complex formed by the two components to gain an insight into how the self-assembled complexes spatially organise within the sample-spanning networked gelator structure. We employed ^{1}H NMR spectroscopy to determine the molar ratio of dendron/diamine present in the immobilised gel network as the molar ratio of the components was incrementally changed (Figure 3). We based our approach on methodology previously published in the literature.[28] It is assumed that gelator incorporated and immobilised within the "solid-like" network cannot be observed in the ^{1}H NMR spectrum due to line broadening effects, whilst material present within the "liquid-like" phase has sharp NMR peaks as a consequence of its molecular-scale mobility. The mobile material can thus be quantified by integration of the peaks and comparison with an internal standard (in this case diphenylmethane) which does not associate with the gel-phase network. In this way, the composition of the immobile networked gelator fibres which underpin the gel can be deduced (Figure 3).

As Figure 3 indicates, irrespective of the molar ratio actually employed, the molar ratio immobilised in the networked gel structure was always ≈1:1 dendron/diamine. This provides strong evidence that a dendron/diamine ratio of 1:1 is optimum for satisfying the spatial requirements of the diamine spacer unit, whilst promoting intermolecular hydrogen bonding between dendritic head groups. The excess diamine was unincorporated within the "solid-like" networked gelator, being instead observed in the "liquid-like" mobile phase.

We then investigated these gels further by variable temperature NMR methods. At 80 °C, in the solution state, both dendron and diamine were clearly observable in the NMR spectrum (Figure 4). At lower temperatures, however, the gel formed, and the resonances associated with the dendron disappeared—only peaks associated with the excess diamine present in the "liquid-like" phase were observed. Furthermore, the resonances associated with diamine **1,4-CH** shifted upfield on decreasing the temperature. At 80 °C, the diamine is complexed by the dendron in solution (although the complex is unable to underpin gelation), but at lower temperatures, the diamine observed by NMR is only the mobile uncomplexed diamine, as the complexed diamine becomes incorporated into the gel. The upfield shift associated with decomplexation indicates that the interaction of **G2-COOH** with **1,4-CH** most likely involves proton transfer (i.e., acid–base interaction between the carboxylic acid and one of the amines). The NMR shifts were less significant for **1,4-BZ**

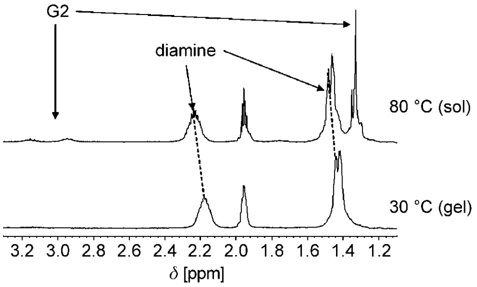

Figure 4. ^{1}H NMR spectra for the system **G2-COOH/1,4-CH**, molar ratio 1: 1.3. [dendron] = 18 mM, solvent = toluene.

than **1,4-CH**, in accordance with the reduced basicity of aromatic amines.

We then employed circular dichroism (CD) spectroscopy to probe the nanoscale chiral organisation.[29] This investigation was performed in the dilute state at a concentration of 3 mM (i.e., below the gelation threshold) in cyclohexane. Under these conditions, CD spectroscopy probes the chiral organisation of the short supramolecular oligomers which are formed before the sample-spanning network is fully assembled.

In previous gels based on **G2-COOH** we have observed thermally responsive CD bands with λ_{max} values at about 220–225 nm, ascribable to chiral organisation of the peptide groups in the dendritic building block.[16–19] The chiral building block, **G2-COOH**, does not exhibit significant CD bands in its own right. On addition of **1,4-BZ** a remarkable and distinctive CD response was observed (Figure 5). A negative CD band was observed at about 215 nm, a positive band at about 230 nm and a negative band at about 255 nm. This CD response can be rationalised as consisting of contributions from nanoscale peptide chiral organisation (at shorter wavelength) as well as chiral organisation of the aromatic **1,4-BZ** unit (at longer wavelength). This is a supramolecular induced circular dichroism effect,[30] in which chiral information is transferred from the dendritic branch to the aromatic diamine within the self-assembled nanoscale chiral architecture.

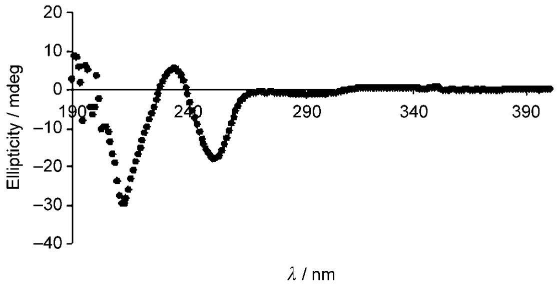

Figure 5. CD spectra of the dendritic branch with the presence of 1,4-diaminobenzene at room temperature. Solvent = cyclohexane; [dendron] = 3 mM.

Conversely, the addition of **1,4-CH** to **G2-COOH** did not induce any chiral ordering (Figure 6). It may have been expected that a CD band associated with chiral organisation of the peptide groups in **G2-COOH** would be observed, however this was not the case. This highlights the subtle interplay between self-assembled, gelator components and the spatial and geometrical requirements necessary for transcription of chiral molecular information into chiral nanoscale assemblies.

The precise spatial organisation of the networked gelator molecules was probed further by small angle neutron scattering (SANS).[31] In all cases, the characteristic dimensions of the scattering objects could be deduced by fitting to a form factor calculated according to infinitely long flexible filaments with a circular cross-section.[21] Figure 7 shows a typical scattering profile and the extracted parameters are shown in Table 1.

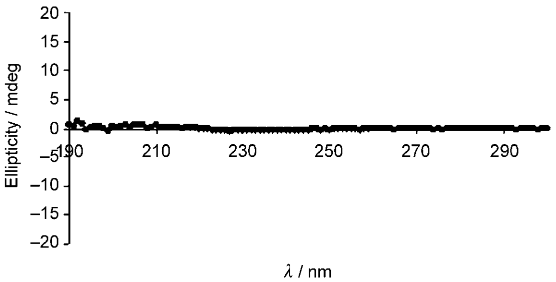

Figure 6. CD spectra of the dendritic branch with the presence of 1,4-diaminocyclohexane at room temperature. Solvent = cyclohexane; [dendron] = 3 mM.

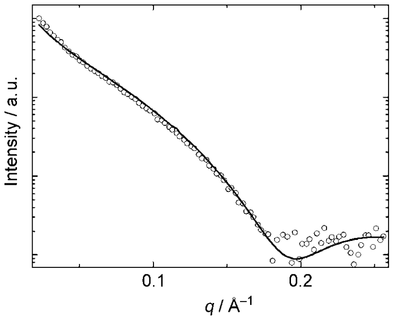

Figure 7. Fitting of the SANS data for **G2-COOH/1,4-BZ**, according to filament objects with a circular cross section.[21]

The data indicate that for **G2-COOH/1,4-CH** 1:1, R_c = 32 Å, with a polydispersity of 25 %. Computer simulations for a single gelator building block predict a 35–40 Å length and a thickness of 20 Å (Figure 8A). It is therefore possible to argue that the circular section of **G2-COOH/1,4-CH** 1:1 filament presents two molecules lying end-by-end across the radial direction. This model is shown in Figure 8B. In this model, intermolecular hydrogen bonds lie along the filament direction explaining the anisotropic nature of the self-assembled state that underpins the networked-gel structure. Importantly, the scattering data for the same gelator system at

Table 1. Parameters used to model the scattering data according to a filament model with a circular cross section.

Sample	Molar ratio	R_c [Å]	σ/R_c [%]	A	B	C
G2-COOH/1,4-CH	1:1	32	25	1×10^{-5}	3	1×10^{-3}
G2-COOH/1,4-CH	1:3.5	30	25	1×10^{-5}	3	1×10^{-3}
G2-COOH/1,4-BZ	1:1	20	16	–	–	–
G2-COOH/1,4-BZ	1:3.5	20	16	–	–	–

a 1:3.5 molar ratio indicated that the R_c value was essentially identical ($R_c = 30$ Å) to the 1:1 molar ratio system, providing conclusive evidence that the self-assembled filaments assembled from the networked gelator are identical in both systems, independent of the amount of diamine present. This effect was also apparent for **G2-COOH/1,4-BZ** system in which R_c values were independent of the total amount of **1,4-BZ** present. For a molar ratio of 1:1, $R_c = 20$ Å; the same as that obtained for a molar ratio of 1:3.5. It is interesting to note that the fibrillar objects formed with **1,4-BZ** are smaller than those formed from **1,4-CH**—indeed, they are approximately the size of an individual 1:1 filament (Figure 8A) This more controlled fibre diameter may help explain why there is greater fidelity in the transcription of chiral information in the former system.

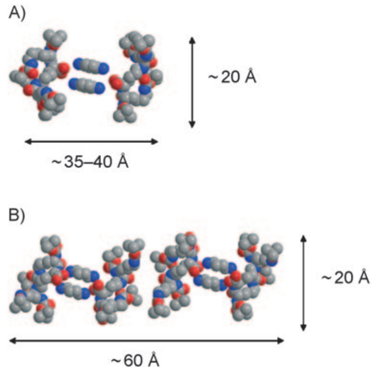

Figure 8. Dimensions and possible self-assembly behaviour of **G2-COOH/1,4-CH** 1:1 based on experimental NMR spectroscopy and SANS data. Modelled using Macromodel 9.5 program (Maestro 8 interface). a) CPK model of the single **G2-COOH/1,4-CH** 1:1 gelator building block; b) a proposed self-assembly model.

In summary, probing the gel on the macroscopic level (T_{gel}), the molecular level (NMR) and the nanoscale level (CD/SANS) led in each case to the same conclusion: for these short rigid "spacer" units, a 1:1 two-component complex is formed in preference to the expected 2:1 complex. This 1:1 complex underpins the formation of the gel network, with excess diamine being tolerated in the "liquid-like" phase to a certain extent (up to ca. 1:4 ratio).

Component selection within complex mixtures: We have recently been interested in assembly from complex mixtures.[23] Cases where specific systems assemble in a controlled way from complex mixtures can be considered as "self-sorting"—a key frontier of supramolecular science.[22] The amenability of these gelators to NMR investigation, the subtle tunability of the two structural components, combined with the stoichiometric fidelity and ability of these gels to tolerate an excess of diamine building block, made them an ideal test-bed to investigate component-selective self-assembly processes.

We investigated a system based on a mixture of **G2-COOH/1,4-BZ/1,3-BZ/1,2-BZ** in a 1:1:1:1 molar ratio in toluene. Once again, we employed NMR methods, with peak integration referenced to diphenylmethane, to determine the amount of gelator present in the "liquid-like" phase and hence deduce the amount of gelator associated with the immobilised, "solid-like" gel network. Figure 9 illustrates how the NMR resonances associated with **1,2-BZ**, **1,3-BZ** and **1,4-BZ** could be readily differentiated. It is clear that in the gel-phase the resonance associated with **1,4-BZ** is the smallest, indicating the least amount of material in the "liquid-like" phase, and therefore the most incorporation into the gel. Table 2 quantifies this, and reports the molar ratios of each diamine which were effectively immobilised in the "solid-like" gel-phase network. For a freshly made sample of gel, NMR integration indicated that 77% of **1,4-BZ** was immobilised within the networked gel, while for **1,3-BZ** and **1,2-BZ** this fell to 21 and only 8%, respectively. Clearly, **1,4-BZ** is selectively incorporated into the gel-phase network and the assembly process is component-selective. We allowed a sample to equilibrate over a period of two weeks, and although small changes in the distribution of diamines in the networked "solid-like" phase were observed, the basic principle remained the same, that is, gels assembled

Table 2. Composition of 'solid-like' networked gelator formed by a mixture of dendron, **1,4-BZ**, **1,3-BZ**, and **1,2-BZ** in a 1:1:1:1 molar ratio at 30 °C in toluene. [Dendron] = 18 mM.

t	Molar fraction of **1,4-BZ** in network	Molar fraction of **1,3-BZ** in network	Molar fraction of **1,2-BZ** in network
fresh	0.771	0.211	0.079
3 d	0.783	0.192	0.116
6 d	0.708	0.268	0.079
13 d	0.708	0.261	0.106

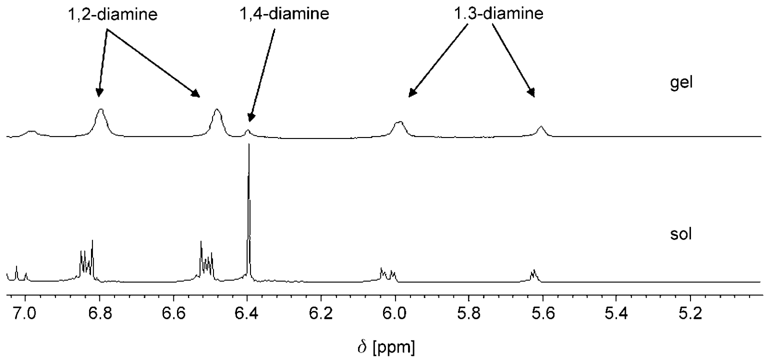

Figure 9. ^{1}H NMR spectra of equimolar mixtures of **1,2-BZ**, **1,3-BZ** and **1,4-BZ**. Top: Gel-state, that is, with dendron **G2-COOH**, [dendron] = 18 mM; bottom: Solution-state, that is, without dendron **G2-COOH**. Solvent = toluene; $T = 30$ °C.

from mixtures preferentially amplified specific components in the gel-phase network.

We argue that the ability of this gelation system to tolerate excess amounts of diamine in the mobile "liquid-like" phase plays a key role in allowing the self-organisation and component-selection process to take place—that is, the excess of unincorporated diamine does not disrupt the gel-forming process. This experiment importantly demonstrates that hierarchical multicomponent self-assembly processes can amplify selected components from complex mixtures, incorporating them into nanostructured assemblies with useful materials properties. These observations are important in the emerging field of systems chemistry,[32] and it is intriguing to consider that this type of "informed" recognition process may have been important in prebiotic chemistry.

Given the ability of this gelator to tolerate unincorporated species in the "liquid-like" phase, we also became interested in the ability of these gels to act as hosts for a ternary guest molecule.[11] To exemplify this principle, we studied the interaction between pyrene and the two-component networked gel. Pyrene was chosen as it has a large π-system which could potentially interact with the **G2-COOH/1,4-BZ** gel as a consequence of π–π interactions. Furthermore, pyrene is readily soluble in toluene and presents readily resolved NMR signals. We employed ^{1}H NMR relaxation studies[33] to investigate the interaction of pyrene with the two different gels (**G2-COOH/1,4-BZ** and **G2-COOH/1,4-CH**) in order to assess the relative selectivities of the different gel networks for this ternary guest.

Table 3 presents the transverse ^{1}H NMR relaxation times for the singlet-like resonance of pyrene. Clearly in both gel systems, pyrene experienced a degree of interaction with the gel network, leading to a decrease in the relaxation time being observed. Most interestingly, the gel network based on **1,4-BZ** caused a greater reduction in the relaxation time than that based on **1,4-CH**. It could be argued that this represents the fact that pyrene forms stronger interactions with the gel network based on **1,4-BZ** than that based on **1,4-CH** and therefore has lower mobility within the former network. This can be rationalised on the basis that **1,4-CH**, unlike **1,4-BZ**, does not contain a π-system and, as a consequence, will be unable to form π–π interactions and hence is expected to show weaker interactions with the pyrene ternary guest.

Table 3. Transverse (T_2) ^{1}H NMR relaxation times measured for systems based on 1:1 molar ratio of networked gelators. [dendron] = 18 mM, Solvent = toluene.

Sample	Pyrene (singlet-like ^{1}H) T_2 [s]
pyrene solution	4.95 ± 0.45
G2/1,4-CH + pyrene	1.65 ± 0.13
G2/1,4-BZ + pyrene	0.75 ± 0.05

We also measured nuclear Overhauser enhancements (NOE) for these systems. Intramolecular NOEs between pyrene protons are positive for "free" pyrene in solution but negative in the presence of the **G2-COOH/1,4-BZ** gel network. This confirms that an exchange process occurs between solvated pyrene molecules and the "solid-like" gel-phase network.

These results support the concept that networked two-component gelators may be exploited as hosts for ternary guests, and that a degree of selectivity is possible based on subtle differences in the molecular-scale structures of the gelator building blocks. This is therefore a promising approach for the development of selective responsive two-component gel-phase materials with applications in sensor technology.[34]

Gel-phase materials which can exhibit component selection have great potential for the selective adsorption and/or sensing of target analytes. Gels are highly porous materials, and diffusion of molecular-scale objects through a nanoscale gel matrix is relatively fast. As such, gel-phase materials which interact selectively with specific species may be of great use in flow-through chromatography applications as well as in the development of "wet" sensors, which are highly compatible with analytes in solution.[35]

Conclusion

In this paper, two-component gelators based on rigid diamines and dendritic acids have been fully characterised and surprisingly, in all cases, irrespective of the molar ratio employed, the dendron/diamine molar ratio in the "solid-like" fibres is 1:1. This stoichiometric control highlights the precise geometrical and spatial arrangement necessary for fibrillar growth and network formation. Intriguingly, when an aromatic diamine was employed, the assembled nanostructure evolved a distinctive chiral signature in the CD spectrum, but when an aliphatic cyclic diamine analogue was used, the self-assembled nanostructure appeared achiral.

The ability of the gel network to tolerate an excess of the diamine led us to explore the self-assembly of networked gelators from mixtures of diamine building blocks, in order to determine whether preferential hierarchical self-assembly could lead to the amplification of specific components within the gel network. We found that when one molar equivalent of the dendron was mixed with an equimolar mixture of 1,2-, 1,3- and 1,4-diaminobenzene, component-selective self-assembly in favour of 1,4-diaminobenzene was observed. In addition, the selectivity of different networked gelator systems towards pyrene as a ternary guest molecule was investigated, and the results suggested that the networked gelator system based on the dendron combined with 1,4-diaminobenzene showed a greater degree of interaction with pyrene than that based on 1,4-diaminocyclohexane.

In summary, we have demonstrated that this gelation system undergoes high fidelity self-assembly with stoichiometric control and component selection/amplification—such principles are of general importance in the organisation of ordered systems from complex mixtures and will underpin the future development of highly responsive and smart soft materials.

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[1] *Organic Nanostructures* (Eds.: J. L. Atwood, J. W. Steed), Wiley-VCH, Weinheim, **2008**.

[2] a) A. R. Hirst, B. Escuder, J.-F. Miravet, D. K. Smith, *Angew. Chem.* **2008**, *120*, 8122–8139; *Angew. Chem. Int. Ed.* **2008**, *47*, 8002–8018; b) N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821–836.

[3] a) *Molecular Gels; Materials with Self-Assembled Fibrillar Networks* (Eds.: R. G. Weiss, P. Terech), Springer, Dordrecht, **2006**; b) D. K. Smith, *Molecular Gels—Nanostructured Soft Materials in Organic Nanostructures* (Eds.: J. L. Atwood, J. W. Steed), Wiley-VCH, Weinheim, **2008**.

[4] For a review of two-component gels see: A. R. Hirst, D. K. Smith, *Chem. Eur. J.* **2005**, *11*, 5496–5508.

[5] For selected examples of two-component gels based on hydrogen bonding and acid–amine interactions: a) K. Hanabusa, T. Miki, Y. Taguchi, T. Koyama, H. Shirai, *J. Chem. Soc. Chem. Commun.* **1993**, 1382–1384; b) K. Inoue, Y. Ono, Y. Kanekiyo, T. Ishi-i, K. Yoshihara, S. Shinkai, *J. Org. Chem.* **1999**, *64*, 2933–2937; c) X. Xu, M. Ayyagari, M. Tata, V. T. John, G. L. McPherson, *J. Phys. Chem.* **1993**, *97*, 11350–11353; d) M. Tata, V. T. John, Y. Y. Waguespack, G. L. McPherson, *J. Am. Chem. Soc.* **1994**, *116*, 9464–9470; e) B. A. Simmons, C. E. Taylor, F. A. Landis, V. T. John, G. L. McPherson, D. K. Schwartz, R. Moore, *J. Am. Chem. Soc.* **2001**, *123*, 2414–2421; f) H. M. Willemen, T. Vermonden, A. T. M. Marcelis, E. J. R. Sudhölter, *Langmuir* **2002**, *18*, 7102–7106; g) M. de Loos, J. van Esch, R. M. Kellogg, B. L. Feringa, *Angew. Chem.* **2001**, *113*, 633-636; *Angew. Chem. Int. Ed.* **2001**, *40*, 613–616; h) K. Nakano, Y. Hishikawa, K. Sada, M. Miyata, K. Hanabusa, *Chem. Lett.* **2000**, 1170–1171; i) G. M. Dykes, D. K. Smith, *Tetrahedron* **2003**, *59*, 3999–4009; j) J. G. Hardy, A. R. Hirst, D. K. Smith, C. Brennan, I. Ashworth, *Chem. Commun.* **2005**, 385–387; k) M. Suzuki, H. Saito, H. Shirai, K. Hanabusa, *New J. Chem.* **2007**, *31*, 1654–1660.

[6] For selected examples of two-component gels based on donor–acceptor interactions: a) U. Maitra, P. V. Kumar, N. Chandra, L. J. D′Sousa, M. D. Prasanna, A. R. Raju, *Chem. Commun.* **1999**, 595–596; b) A. Friggeri, O. Gronwald, K. J. C. van Bommel, S. Shinkai, D. N. Reinhoudt, *J. Am. Chem. Soc.* **2002**, *124*, 10754–10758; c) P. Babu, N. M. Sangeetha, P. Vijaykumar, U. Maitra, K. Rissanen, A. R. Raju, *Chem. Eur. J.* **2003**, *9*, 1922–1932; d) B. G. Bag, G. C. Maity, S. K. Dinda, *Org. Lett.* **2006**, *8*, 5457–5460; e) J. R. Moffat, D. K. Smith, *Chem. Commun.* **2008**, 2248–2250.

[7] For selected examples of two-component gels based on ligand–metal interactions: a) M. Enomoto, A. Kishimura, T. Aida, *J. Am. Chem. Soc.* **2001**, *123*, 5608–5609; b) A. Kishimura, T. Yamashita, T. Aida, *J. Am. Chem. Soc.* **2005**, *127*, 179–183; c) A. Ghoussoub, J.-M. Lehn, *Chem. Commun.* **2005**, 5763–5765; d) M. Shirakawa, N. Fujita, T. Tani, K. Kaneko, S. Shinkai, *Chem. Commun.* **2005**, 4149–4151; e) S. Kume, K. Kuroiwa, N. Kimizuka, *Chem. Commun.* **2006**, 2442–2444; f) A. Y.-Y. Tam, K. M.-C. Wong, G. Wang, V. W.-W. Yam, *Chem. Commun.* **2007**, 2028–2030; g) U. Hahn, A. R. Hirst, J. L. Delgado, A. Kaeser, B. Delavaux-Nicot, J.-F. Nierengarten, D. K. Smith, *Chem. Commun.* **2007**, 4943–4945.

[8] For selected examples of two-component gels based on reversible chemical reactions: a) M. George, R. G. Weiss, *Langmuir* **2003**, *19*, 1017–1025; b) M. George, R. G. Weiss, *Langmuir* **2002**, *18*, 7124–7135.

[9] a) A. R. Hirst, D. K. Smith, M. C. Feiters, H. P. M. Geurts, A. C. Wright, *J. Am. Chem. Soc.* **2003**, *125*, 9010–9011; b) A. R. Hirst, D. K. Smith, J. P. Harrington, *Chem. Eur. J.* **2005**, *11*, 6552–6559.

[10] H. Y. Lee, S. R. Nam, J-I. Hong, *J. Am. Chem. Soc.* **2007**, *129*, 1040–1041.

[11] P. Mukhopadhyay, Y. Iwashita, M. Shirakawa, S.-I. Kawano, N. Fujita, S. Shinkai, *Angew. Chem.* **2006**, *118*, 1622–1625; *Angew. Chem. Int. Ed.* **2006**, *45*, 1592–1595.

[12] C. E. Stanley, N. Clarke, K. M. Anderson, J. A. Elder, J. T. Lenthall, J. W. Steed, *Chem. Commun.* **2006**, 3199–3201.

[13] S. J. Brignell, D. K. Smith, *New J. Chem.* **2007**, *31*, 1243–1249.

[14] For selected examples see: a) K. J. C. van Bommel, C. van der Pol, I. Muizebelt, A. Friggeri, A. Heeres, A. Meetsma, B. L. Feringa, J. van Esch, *Angew. Chem.* **2004**, *116*, 1695–1699; *Angew. Chem. Int. Ed.* **2004**, *43*, 1663–1667; b) Y. Zhang, H. Gu, Z. Yang, B. Xu, *J. Am. Chem. Soc.* **2003**, *125*, 13680–13681; c) J. E. A. Webb, M. J. Crossley, P. Turner, P. Thordarson, *J. Am. Chem. Soc.* **2007**, *129*, 7155–7162; d) Z. Dzolic, M. Cametti, A. D. Cort, L. Mandolini, M. Zinic, *Chem. Commun.* **2007**, 3535–3537; e) W. Deng, H. Yamaguchi, Y. Takshima, A. Harad, *Angew. Chem.* **2007**, *119*, 5236–5239; *Angew. Chem. Int. Ed.* **2007**, *46*, 5144–5147; f) M. Yamanaka, T. Nakamura, T. Nakagawa, H. Itagaki, *Tetrahedron Lett.* **2007**, *48*, 8990–8993.

[15] D. K. Smith, *Chem. Commun.* **2006**, 34–44.

[16] A. R. Hirst, D. K. Smith, M. C. Feiters, H. P. M. Geurts, *Langmuir* **2004**, *20*, 7070–7077.

[17] A. R. Hirst, D. K. Smith, *Org. Biomol. Chem.* **2004**, *2*, 2965–2971.

[18] A. R. Hirst, D. K. Smith, *Langmuir* **2004**, *20*, 10851–10857.

[19] A. R. Hirst, D. K. Smith, M. C. Feiters, H. P. M. Geurts, *Chem. Eur. J.* **2004**, *10*, 5901–5910.

[20] J. G. Hardy, A. R. Hirst, I. Ashworth, C. Brennan, D. K. Smith, *Tetrahedron* **2007**, *63*, 7397–7406.

[21] A. R. Hirst, I. A. Coates, T. Boucheteau, B. Escuder, J.-F. Miravet, V. Castelletto, I. W. Hamley, D. K. Smith, *J. Am. Chem. Soc.* **2008**, *130*, 9113–9121.

[22] For selected examples of self-sorting processes see: a) R. Kramer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* **1993**, *90*, 5394–5398; b) S. J. Rowan, D. G. Hamilton, P. A. Brady, J. K. M. Sanders, *J. Am. Chem. Soc.* **1997**, *119*, 2578–2579; c) P. N. Taylor, H. L. Anderson, *J. Am. Chem. Soc.* **1999**, *121*, 11538–11545; d) B. Bilgicer, X. Xing, K. Kumar, *J. Am. Chem. Soc.* **2001**, *123*, 11815–11816; e) I. W. Hwang, T. Kamada, T. K. Ahn, D. M. Ko, T. Nakamura, A. Tsuda, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2004**, *126*, 16187–16198; f) S. G. Telfer, T. Sato, R. Kuroda, J. LeFebvre, D. B. Leznoff, *Inorg. Chem.* **2004**, *43*, 421–429; g) A. X. Wu, L. Isaacs, *J. Am. Chem. Soc.* **2003**, *125*, 4831–4835; h) P. Mukhopadhyay, A. Wu, L. Isaacs, *J. Org. Chem.* **2004**, *69*, 6157–6164; i) N. A. Schnarr, A. J. Kennan, *J. Am. Chem. Soc.* **2003**, *125*, 667–671; j) N. Sreenivasachary, J.-M. Lehn, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 5938–5943; k) S. M. Liu, C. Ruspic, P. Mukhopadhyay, S. Chakrabarti, P. Y. Zavalij, L. Isaacs, *J. Am. Chem. Soc.* **2005**, *127*, 15959–15967; l) I. Saur, R. Scopelliti, K. Severin, *Chem. Eur. J.* **2006**, *12*, 1058–1066; m) C. Burd, M. Weck, *Macromolecules* **2005**, *38*, 7225–7230; n) P. Mukhopadhyay, P. Y. Zavalij, L. Isaacs, *J. Am. Chem. Soc.* **2006**, *128*, 14093–14102; o) N. Severin, I. M. Sokolov, N. Miyashita, D. G. Kurth, J. P. Rabe, *Macromolecules* **2007**, *40*, 5182–5186; p) M. K. Khan, P. R. Sundararaian, *J. Phys. Chem. B* **2008**, *112*, 4223–4232; q) D. Braekers, C. Peters, A. Bogdan, Y. Rudzevich, V. Böhmer, J. F. Desreux, *J. Org. Chem.* **2008**, *73*, 701–706.

[23] a) A. R. Hirst, B. Huang, V. Castelletto, I. W. Hamley, D. K. Smith, *Chem. Eur. J.* **2007**, *13*, 2180–2188; b) J. R. Moffat, D. K. Smith, *Chem. Commun.* **2008**, DOI: 10.1039/b818058j.

[24] a) G. M. Dykes, L. J. Brierley, D. K. Smith, P. T. McGrail, G. J. Seeley, *Chem. Eur. J.* **2001**, *7*, 4730–4739; b) M. Driffield, D. M. Goodall, D. K. Smith, *Org. Biomol. Chem.* **2003**, *1*, 2612–2620; c) G. M. Dykes, D. K. Smith, A. Caragheorgheopol, *Org. Biomol. Chem.* **2004**, *2*, 922–926.

[25] H. C. Brown, D. H. McDaniel, O. Häflinger in *Determination of Organic Structures by Physical Methods* (Eds.: E. A. Braude, F. C. Nachod), Academic Press, New York, **1955**.

[26] S. R. Raghavan, B. H. Cipriano, *Gel Formation: Phase Diagrams using Tabletop Rheology and Calorimetry in Molecular Gels, Materials with Self-Assembled Fibrillar Networks* (Eds.: R. G. Weiss, P. Terech), Springer, Dordrecht, **2006**, chap. 8.

[27] Y. Y. Waguespack, S. Banerjee, P. Ramannair, G. C. Irvin, V. T. John, G. L. McPherson, *Langmuir* **2000**, *16*, 3036–3041.

[28] B. Escuder, M. Llusar, J.-F. Miravet, *J. Org. Chem.* **2006**, *71*, 7747–7752.

[29] For an overview of CD spectroscopy see: N. Berova, K. Nakanishi, R. W. Woody, *Circular Dichroism: Principles and Applications*, 2nd ed., Wiley-VCH, Weinheim, **1994**.

[30] For a review see: a) S. Allenmark, *Chirality* **2003**, *15*, 409–422; For selected examples see: b) H. Engelkamp, S. Middelbeek, R. J. M. Nolte, *Science* **1999**, *284*, 785–788; c) C. Thalacker, F. Würthner, *Adv. Funct. Mater.* **2002**, *12*, 209–218; d) T. Miyagawa, M. Yamamoto, R. Muraki, H. Onouchi, E. Yashima, *J. Am. Chem. Soc.* **2007**, *129*, 3676–3682; e) Y. Li, T. Wang, M. Liu, *Soft Matter* **2007**, *3*, 1312–1317.

[31] O. Glatter, O. Kratky, *Small Angle X-ray Scattering*, Academic Press, London **1982**.

[32] R. F. Ludlow, S. Otto, *Chem. Soc. Rev.* **2008**, *37*, 101–108.

[33] D. C. Duncan, D. G. Whitten, *Langmuir* **2000**, *16*, 6445–6452.

[34] X. Salvatella, E. Giralt, *Chem. Soc. Rev.* **2003**, *32*, 365–372.

[35] a) I. Yoshimura, Y. Miyahara, N. Kasagi, H. Yamane, A. Ojida, I. Hamachi, *J. Am. Chem. Soc.* **2004**, *126*, 12204–12205; b) S. Yamaguchi, I. Yoshimura, T. Kohira, S.-i. Tamaru, I. Hamachi, *J. Am. Chem. Soc.* **2005**, *127*, 11835–11841.

Received: July 21, 2008