ChemComm

Supramolecular dendritic two-component gel

Kevin S. Partridge,[a] David K. Smith,*[a] Graham M. Dykes[a] and P. Terry McGrail[b]

[a] *Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: dks3@york.ac.uk*
[b] *ICI Technology, PO Box 90, Wilton Centre, Middlesbrough, Cleveland, UK TS90 8JE*

Received (in Cambridge, UK) 4th December 2000, Accepted 16th January 2001
First published as an Advance Article on the web 31st January 2001

Dendritic peptides with a carboxylic acid at the focal point of the branched structure form a two-component supramolecular organogel with a linear aliphatic diamine in non-hydrogen-bonding solvents.

There has been intense interest in the development of efficient and tunable small molecule gelators for organic solvents,[1] partly because gels possess many varied industrial applications as a consequence of the diversity of gel structures on both a microscopic and mesoscopic scale. Multiple supramolecular interactions[2] between the individual building blocks are critical in the gel forming process—for example hydrogen bonding, metal coordination, hydrophobicity *etc.* The ability of dendritic structures to act as gelators has, as a consequence of their multiplicity of functional groups, been of some interest. Newkome and co-workers reported dendrimers with a hydrophilic periphery and a hydrophobic core which stacked in aqueous solution, forming a gel.[3] Aida and co-workers reported a dendritic branch functionalised with a dipeptide at the focal point, which gelated organic solvents primarily through hydrogen bonding interactions.[4] In addition, Beginn and co-workers described branched amphiphiles functionalised with long aliphatic chains which gelate organic solvents.[5]

Recently, there has been increasing interest in the development of two-component gelling systems in which the presence of two complementary building blocks in solution is essential in order for gel formation to occur.[6–8] In these cases, supramolecular interactions between the complementary units allow a complex to form which is then capable of assembling further *via* inter-complex interactions to form the fully gelated network. Reports of two-component systems are still limited, and in this communication we report for the first time a controllable two-component dendritic system which gelates organic solvents as a consequence of specific supramolecular interactions.[9]

We recently reported the use of dendritic branches **1**, **2** and **3** constructed from L-lysine building blocks using a solution phase approach[10] to solubilise a hydrophilic dye into apolar solvents.[11] It was proposed that these dendritic branches containing a free carboxylic acid unit at the focal point (Fig. 1) interact with molecules containing basic amine sites through the formation of a hydrogen bonded (acid–base) complex with potential proton transfer (and salt bridge formation).[12] We therefore became interested in the ability of this type of dendritic branch to interact with amines possessing different structural motifs, such as long chain aliphatic diamines. We quickly discovered that the combination of dendritic branch **2** and diaminododecane (**4**) was capable of gelating organic solvents (Fig. 2), and we set about discovering the *key criteria required for effective gel formation*.[13]

Neither dendritic branch nor diamine alone are capable of gelating the solvent—branch **2** forms homogeneous solutions up to a concentration of at least 350 mg ml^{-1} (0.44 M), whilst diaminododecane (**4**) is largely insoluble. On mixing a solution of **2** in CH_2Cl_2 and solid **4**, followed by sonication and standing, dissolution of **4** combined with strong gel formation was observed. This indicates that an interaction between **2** and **4** takes place, solubilising **4** into CH_2Cl_2,[11] and that the complex subsequently induces gel formation.

The *concentrations* of dendritic branch **2** and diamine **4** were optimised for the effective gelation of DCM. At low concentrations of dendritic branch **2** (< 20 mg ml^{-1}, < 25 mM), gel formation is largely ineffective, however, above this concentration (> 2.0 wt vol%$^{-1}$) strong gels were observed. In particular, very strong gels were formed at a branch concentration of 25 mg ml^{-1} (31 mM). The strongest gel was observed using 10 mg of solid diaminododecane (**4**). Below a given mass of diamine **4**, however (2.5 mg, 12.5 mM), the diamine was completely solubilised by the dendritic branch, but gel formation would not

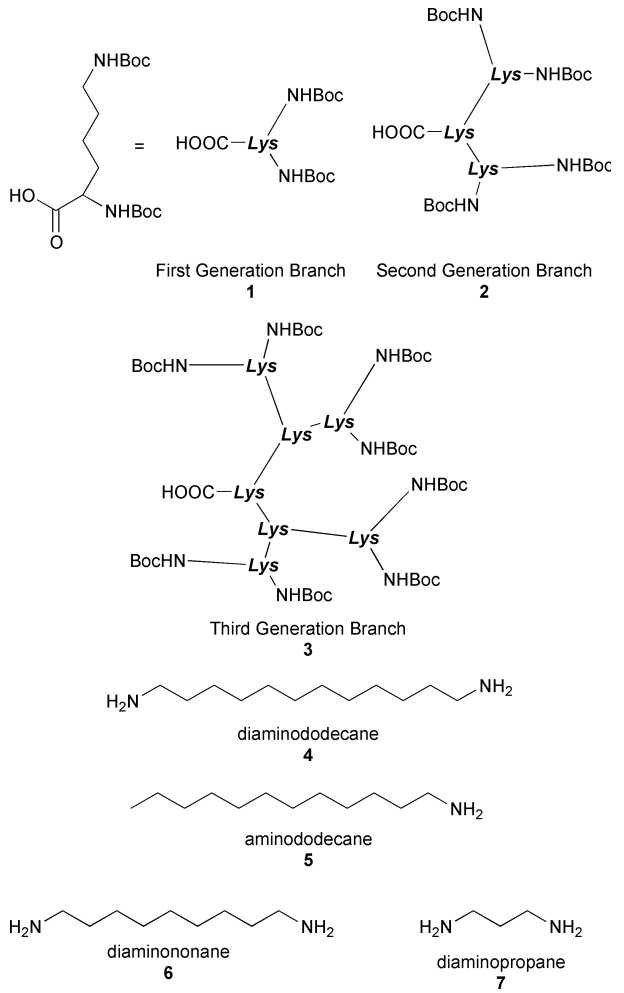

Fig. 1 Dendritic branches (**1**–**3**) and linear aliphatic amines (**4**–**7**) investigated. Combination of certain branches with complementary diamines leads to effective organogel formation.

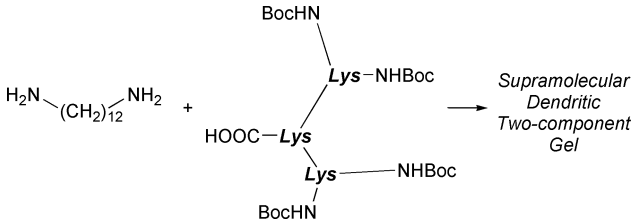

Fig. 2 Dendritic branch **2** solubilises diamine **4** into organic solvents (*e.g.* toluene, CH_2Cl_2 and CH_3CN) and the complex then induces gelation.

DOI: 10.1039/b009672p

Table 1 Effect of solvent on gel formation by compounds **2** (25 mg ml^{-1}, 31 mM) and **4** (10 mg). The Kamlet-Taft α and β parameters (relating to the ability of the solvent to donate and accept hydrogen bonds respectively) are also shown

Solvent	α (H-bond donor ability)	β (H-bond acceptor ability)	Gel formation using branch **2** and diamine **4** (25 mg ml^{-1} and 10 mg, respectively)
Toluene	0.00	0.11	Yes—rapid
Acetone	0.08	0.48	Solvent reacts with amine
CH_3CN	0.19	0.31	Yes—rapid, very strong gels
CH_2Cl_2	0.30	0.00	Yes—slow
$CHCl_3$	0.44	0.00	No
MeOH	0.93	0.62	No

readily occur. It is interesting to note that gelation becomes difficult when the molar ratio of diamine–branch falls below 1:2 and this result indicates that controlling the relative amounts of the two components is important. This would be expected if both components are complementary and essential for gel formation.

The *structure of the dendritic branch* was subsequently varied. First generation dendritic branch **1** did not induce gel formation with diaminododecane (**4**) at any concentration investigated (10–50 mg ml^{-1}, (29–145 mM) [**1**], 1–20 mg, (5–100 mM) [**4**]). This indicates that the dendritic branching of compound **2** plays a key role in enabling gelation to occur. Third generation dendritic branch **3** showed similar behaviour to second generation branch **2**, forming strong gels at 25 mg ml^{-1} (14.5 mM) with diaminododecane (4.5 mg). Interestingly, although the mass of **3** required to gelate the solution was the same as the mass of **2**, this is a lower absolute concentration (14.5 mM—as compared to 31 mM required for compound **2**) as a consequence of the higher molecular mass of the third generation branch. In a control experiment, branch **2** was protected at the focal point as a methyl ester. In this case, no solubilisation of diaminododecane occurred and furthermore, there was no gel formation. This indicates the importance of complementary interactions between carboxylic acid and amine as previously reported for dye solubilisation.[11]

The *structure of the aliphatic diamine* is also important in controlling gel formation. If a monoamine (aminododecane, **5**) was used, no gelation occurred in CH_2Cl_2, even at almost double the concentration of dendritic branch (40 mg ml^{-1}, 50 mM). If a shorter aliphatic diamine (diaminononane, **6**) was used, gelation with branch **2** was less successful, whilst using diaminopropane (**7**) led to no gel formation at all. This indicates the importance of having a sufficiently long aliphatic chain for gelation to occur. Interestingly, however, first generation branch **1** did form a weak gel with diaminononane (**6**) in CH_2Cl_2, although not with any other diamine. This could indicate that it is important to tune the length of the aliphatic diamine to match the generation of the dendritic branching for optimal gel formation. These results clearly illustrate the importance of microscopic structural features in controlling the macroscopic properties of the supramolecular dendritic gel.[14]

The *effect of solvent* on the gelation of **2** and **4** was then investigated (Table 1). The best solvent for gel formation appeared to be CH_3CN in which gelation occurred very rapidly, even at dendritic branch concentrations as low as 15 mg ml^{-1} (18.5 mM). Interestingly, gel formation occurred most readily in solvents which possess a low Kamlet-Taft α parameter.[15] This parameter reflects the ability of the solvent to donate hydrogen bonds (*i.e.* to the amine groups). This clearly indicates the importance of hydrogen bonds—competitive interactions from the solvent prevent gelation. Hydrogen bonds (either with or without associated proton transfer) are responsible for the interaction between the carboxylic acid of **2** and the amines of **4**, and may also play important roles in further mediating the gelation (*e.g.* hydrogen bond interactions between peptide groups in the dendritic branching).

In conclusion, we have demonstrated for the first time that suitably functionalised dendritic branches can undergo supramolecular two-component gelation of an organic solvent in the presence of a suitable complementary guest—a process mediated by hydrogen bond interactions. It is hoped in the future to expand the tunability of these gels by varying the structure of the individual components, and hence generate organogels with desirable physical properties. Furthermore the application of these gels to sensing and catalysis will be investigated.

D. K. S. acknowledges the support of the University of York, EPSRC (G. M. D) and ICI Technology (G. M. D.).

Notes and references

1 For excellent overviews of this area see: (*a*) P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133; (*b*) J. H. van Esch and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2000, **39**, 2263 and references therein.

2 For reviews of supramolecular chemistry, see (*a*) P. D. Beer, P. A. Gale, D. K. Smith, *Supramolecular Chemistry*, Oxford University Press, Oxford, 1999; (*b*) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; (*c*) F. Diederich, *Cyclophanes*, The Royal Society of Chemistry, Cambridge, 1991.

3 (*a*) G. R. Newkome, G. R. Baker, M. J. Saunders, P. S. Russo, V. K. Gupta, Z.-q. Yao, J. E. Miller and K. Bouillon, *J. Chem. Soc., Chem. Commun.*, 1986, 752; (*b*) G. R. Newkome, G. R. Baker, S. Arai, M. J. Saunders, P. S. Russo, K. J. Theriot, C. N. Moorefield, L. E. Rogers, J. E. Miller, T. R. Lieux, M. E. Murray, B. Phillips and L. Pascal, *J. Am. Chem. Soc.*, 1990, **112**, 8458; (*c*) G. R. Newkome, C. N. Moorefield, G. R. Baker, R. K. Behera, G. H. Escamilla and M. J. Saunders, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 917; (*d*) G. R. Newkome, X. Lin, C. Yaxiong and G. H. Escamilla, *J. Org. Chem.*, 1993, **58**, 3123.

4 W.-D. Jang, D.-L. Jiang and T. Aida, *J. Am. Chem. Soc.*, 2000, **122**, 3232.

5 (*a*) U. Beginn, *Adv. Mater.*, 1998, **10**, 1391; (*b*) U. Beginn, S. Sheiko and M. Möller, *Macromol. Chem. Phys.*, 2000, **201**, 1008; (*c*) U. Beginn, G. Zipp and M. Möller, *Chem. Eur. J.*, 2000, **6**, 2016.

6 Aminopyridine–isocyanuric acid (hydrogen-bonding interactions): (*a*) K. Hanabusa, T. Miki, Y. Taguchi, T. Koyama and H. Shirai, *J. Chem. Soc., Chem Commun.*, 1993, 1382; (*b*) S. W. Jeong, K. Murata and S. Shinkai, *Supramol. Sci.*, 1996, **3**, 83; (*c*) K. Inoue, Y. Ono, Y. Kanekiyo, T. Ishi-i, K. Yoshihara and S. Shinkai, *J. Org. Chem.*, 1999, **64**, 2933.

7 Phenol–AOT (hydrogen-bond interaction): X. Xu, M. Ayyagari, M. Tata, V. T. John and G. L. McPherson, *J. Phys. Chem.*, 1993, **97**, 11 350 (AOT = sodium bis(2-ethylhexyl)sulfosuccinate).

8 Bile acid-Pyrene–trinitrofluorenone (aromatic donor–acceptor interactions): U. Maitra, P. V. Kumar, N. Chandra, L. J. D'Sousa, M. D. Prasanna and A. R. Raju, *Chem. Commun.*, 1999, 595.

9 For reviews of the growing field of supramolecular dendrimer chemistry see: (*a*) F. W. Zeng and S. C. Zimmerman, *Chem. Rev.*, 1997, **97**, 1681; (*b*) V. V. Narayanan and G. R. Newkome, *Top. Curr. Chem.*, 1998, **197**, 20; (*c*) D. K. Smith and F. Diederich, *Top. Curr. Chem.*, 2000, **210**, 183.

10 (*a*) R. G. Denkewalter, J. Kolc and W. J. Lukasavage, US Patent No. 4 289 872, 1981; assigned to Allied Corp; (*b*) J. P. Tam, *Proc. Natl. Acad. Sci. USA*, 1988, **85**, 5409.

11 D. K. Smith, *Chem. Commun.*, 1999, 1685.

12 For other reports of acid–amine interactions using dendrimers see: (*a*) V. Chechik, M. Zhao and R. M. Crooks, *J. Am. Chem. Soc.*, 1999, **121**, 4910; (*b*) L. J. Twyman, A. E. Beezer, R. Esfand, M. J. Hardy and J. C. Mitchell, *Tetrahedron Lett.*, 1999, **40**, 1743.

13 In a typical gel forming experiment, a sample of the dendritic branch (**1**, **2** or **3**) was dissolved in the organic solvent (1 ml) and to this was added a quantity of solid diaminododecane. The mixture was then sonicated at ambient temperature for 1 hour and allowed to stand. The strength of the gel formed was estimated by a visual investigation of its rheological properties. This involved inversion of the tube containing the gel and checking that neither the gel nor excess solvent ran down the side of the tube, and also lightly shaking the sample to ensure structural integrity was maintained for strong gels.

14 For a paper in which the microscopic structure of the gelator controls its potency see: K. Yoza, N. Amanokura, Y. Ono, T. Akao, H. Shinmori, M. Takeuchi, S. Shinkai and D. N. Reinhoudt, *Chem. Eur. J.*, 1999, **5**, 2722.

15 M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.