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Cation-responsive silver-selective organogel—exploiting silver–alkene interactions in the gel-phase†

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We report a gelator that is responsive to Ag^+ and Li^+ cations but unresponsive to Na^+ and K^+, and demonstrate that silver–alkene interactions play a vital role in mediating the selective gel–sol response to Ag^+.

Supramolecular gels[1] are an intriguing and important class of soft material with many proposed applications in a wide range of fields.[2] They consist of a network, most commonly of nano-scale fibres underpinned by non-covalent interactions between molecular-scale building blocks. The weak nature of these forces imposes a degree of reversibility on gel formation/breakdown which can therefore be triggered by external stimuli, such as temperature, pH, UV irradiation, redox systems, enzymes and ionic species.[1,2]

Gels that bind cations have recently been covered in a very thorough review.[3] Use of Ag^+ has become increasingly common in the formation of self-assembled gels and/or coordination polymers.[4] The vast majority of reports involving Ag^+ in gelation involve coordination between the Ag^+ ion and a donor heteroatom, such as nitrogen or sulfur.[5] There have been a number of reports of cation-responsive gels, in which selected cations lead to gel breakdown, for example, gelators incorporating crown ethers which respond to Group 1 metal cations as a consequence of binding.[6] There are, however, few reports in which a gel is shown to respond to silver cations. In an interesting paper, Thompson and co-workers developed a cyclodextrin based gelator that bound Co^{3+}, Ni^{2+}, Cu^{2+} and Ag^+ through an amine group, leading to a gel–sol transition.[7]

In recent times, attention has begun to focus on the use of Ag^+-alkene interactions[8] as a supramolecular synthon,[9] but they are still, at present, under-exploited in this regard. These interactions have been used in chromatography[10] and NMR shift reagents,[11] however, most recent reports of silver–alkene interactions have been largely restricted to discrete organometallic complexes or assemblies that exist in the solid state.[11] We decided to explore silver–alkene interactions within the gel-phase, and uncover whether such interactions could be used to develop Ag^+-selective responsive gels. This has also allowed us to gain insight into Ag^+–alkene interactions both in the gel-phase and solution.

Our investigation focuses on gelator **G1-ene**, a bolaform gelator with L-lysine head groups and peripheral alkenes, which was previously reported by our group (Fig. 1).[12] This compound is known to form gels as a consequence of gelator–gelator intermolecular hydrogen bond interactions between amides within the peptide 'head groups'. This gelator formed opaque gels in ethyl acetate (Fig. 2, MGC = 0.18 wt%). These gels were tested for their response to a number of salts; $AgSbF_6$, $LiPF_6$, $NaPF_6$ and $KSbF_6$, with an ethyl acetate solution of the salt being gently pipetted onto the pre-formed gel. The gels showed a response to Ag^+ and Li^+ by undergoing a gel–sol transition (Fig. 2), with the gel breaking down from top to bottom as the salt diffuses through the gel. However the gels were completely unresponsive to Na^+ or K^+ (Fig. 2). The gel–sol transition with Ag^+ was far faster (minutes) than with Li^+ (hours) indicating a different rate of interaction between the cation and the gelator fibres. Less Ag^+ (*ca.* 12 mM) was required to break down the gel than Li^+ (*ca.* 90 mM). From this preliminary experiment we concluded that gelator **G1-ene** exhibits an Ag^+/Li^+-selective gel–sol response with enhanced response towards Ag^+. The anions were chosen for reasons of availability/solubility, but the choice of PF_6^- or SbF_6^-, which are analogous to one another, appeared to have no impact on gelation.

To investigate the mechanism of cation response on the molecular scale, these samples were dried under vacuum. The residual solids in the presence of cations were analysed by ATR-FTIR and the resulting spectra compared to that of the pure xerogel of **G1-ene** (Fig. 3 and ESI†). Bands at 993 and 910 cm^{-1} were assigned as

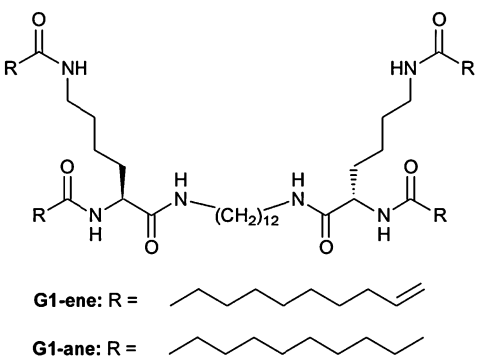

Fig. 1 Gelators synthesized and studied in this paper.

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† Electronic Supplementary Information (ESI) available: synthesis and characterisation, IR spectra, Job plots and titration curves. See DOI: 10.1039/c2cc17854k

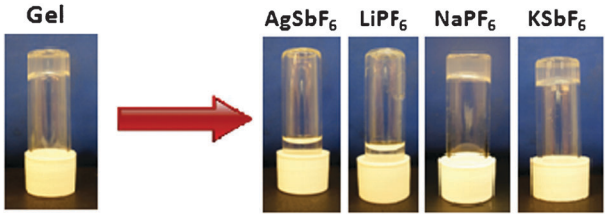

Fig. 2 Response of gels of **G1-ene** in ethyl acetate to solutions of metal salts. All gels are 3 mM, salt solutions are 90 mM, except for $AgSbF_6$ which is 30 mM.

alkene bends and bands at 1633 cm^{-1} and 1535 cm^{-1} as the carbonyl and amide II stretch. On addition of $AgSbF_6$, both alkene bends disappeared and a new band at 949 cm^{-1} was visible, consistent with the formation of an Ag^+–alkene bond (Fig. 3).[13] The carbonyl stretch at 1633 cm^{-1} and amide II band at 1535 cm^{-1} were also shifted, to 1628 and 1547 cm^{-1}. This weakening of C=O and strengthening of amide II (C=N) is indicative of some metal ion binding to the C=O group. The peak at 650 cm^{-1} corresponds to the SbF_6 anion. Importantly, the addition of $LiPF_6$ (see ESI†) caused no significant change in the alkene bands but did induce a similar shift of the carbonyl and amide II bands as $AgSbF_6$, indicative of C=O···Li^+ interactions. When the xerogels of **G1-ene** with $NaPF_6$ and $KSbF_6$ were examined, there was no significant shift in the carbonyl, amide II or alkene bands, suggesting there was no interaction between these cations and gelator **G1-ene**.

NMR was then used to further characterise the metal binding. Gels of **G1-ene** were NMR silent owing to the immobility of the molecules within the gel fibres on the NMR timescale. Furthermore, the solubility of **G1-ene** in other solvents was generally poor. For these reasons, a soluble, small molecule analogue, **1-ene**, was synthesized (Fig. 4). This represents a fragment of **G1-ene** and contains both the amide and alkene groups. Crucially, its enhanced solubility allowed us to probe its interactions with metal ions by NMR methods.

In an initial experiment, two equivalents of each salt were added to a solution of **1-ene** in ethyl acetate and analysed by ^{13}C NMR (Fig. 5). The spectrum in the presence of Ag^+ had significant chemical shift perturbations on both the alkene and the amide functional groups, indicating that this cation bound to both the amide and alkene in solution. The addition of Li^+ perturbed the amide, and led to peak broadening around this peak, which may indicate kinetically slow binding on the NMR timescale, but there was no perturbation of the alkene resonances, indicating no interaction with this group.

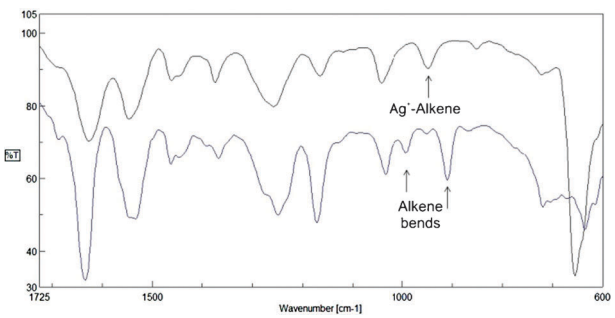

Fig. 3 ATR-FTIR spectra from **G1-ene** xerogel (bottom) and **G1-ene**/$AgSbF_6$ xerogel (top).

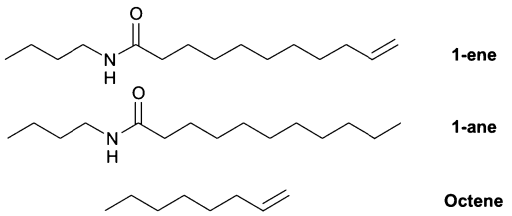

Fig. 4 Model compounds used for the NMR solution-phase studies.

Neither Na^+ nor K^+ led to significant perturbations of the NMR spectrum, indicating they do not interact significantly with **1-ene**. In this way, the NMR was in agreement with IR studies of **G1-ene** described above.

It was plausible that cation complexation to C=O was responsible for gel breakdown. This is a sensible hypothesis as the gel network is underpinned by intermolecular hydrogen bond interactions between the amide (CONH) groups. We therefore synthesised gelator **G1-ane** (Fig. 1), to allow us to determine whether the alkene was playing any active role. Gelator **G1-ane** maintains the bolaform gelator structure, and the hydrogen bonding molecular recognition pathways, but lacks the peripheral alkenes (see ESI†). Gels of **G1-ane** in ethyl acetate were made and treated with the metal salts in exactly the same way as gelator **G1-ene**. The gels were still responsive to Li^+ and still unresponsive to Na^+ and K^+. However, the gels of **G1-ane** were completely unresponsive to Ag^+. This suggests that the Ag^+–alkene interaction must play a vital role in enabling the rapid response of **G1-ene** to Ag^+.

^{13}C NMR titration experiments were employed to observe how the presence of the alkene affects the binding of Ag^+ to the amide and *vice versa*. The binding of $AgSbF_6$ to three compounds (**1-ene**, **1-ane** and **Octene**) (Fig. 4) was studied. Firstly, a Job plot analysis of each compound was carried out (for data see ESI†). When following the alkene resonance for **1-ene** or **Octene** the stoichiometry appeared as predominantly 1 : 1 (with a small contribution from 1 : 2 M : L). However, when following the C=O resonance of **1-ene** or **1-ane**, a very broad Job plot indicating a mix of 1 : 4, 1 : 3 and 1 : 2 complexes was observed. A ^{13}C NMR titration of each compound with $AgSbF_6$ was then carried out (see ESI†). Stability constants were fitted for the alkene carbon resonances with WinEQNMR2[14] using a 1 : 1 stoichiometry, giving *log*K values of 1.8 for **1-ene** and 1.4 for **Octene** (both 15% error), with the chemical shift changes being almost identical. The presence of the amide group in **1-ene** therefore appears to have only a small effect on the interaction

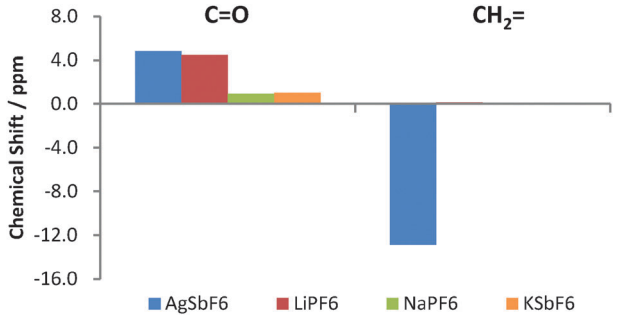

Fig. 5 Change in chemical shift caused to carbonyl and alkene carbon resonances by addition of two equivalents of each metal salt.

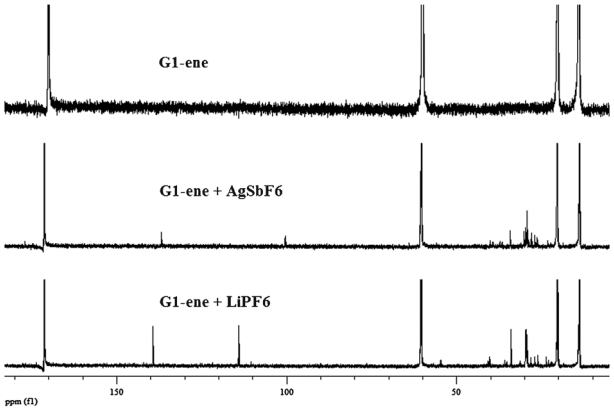

Fig. 6 ^{13}C NMR spectra of **G1-ene** gel in ethyl acetate, and of the gel sample after the addition of $AgSbPF_6$ or $LiPF_6$.

between the alkene and Ag^+, with the binding curves being almost superimposable. Reliable stability constants for amide (C═O) binding to the metal ion could not be fitted to the data, due to the ill-defined complex stoichiometry—however, the binding curves for **1-ene** and **1-ane** indicated that C═O was affected by Ag^+ in roughly the same way for both compounds—compound **1-ene** reached saturation slightly more slowly than **1-ane** which would indicate that binding of Ag^+ to the alkene of **1-ene** occurs prior to C═O binding. These data indicate that in the solution phase, the binding of the alkene and the amide to Ag^+ can both occur. For the binding of **1-ene** to Ag^+ ions, we therefore propose that (i) the alkene acts as the primary binding site (*ca.* 1 : 1 binding) as in **Octene** and, (ii) an ill-defined number of C═O groups can then bind weakly to the alkene-bound Ag^+. In the gel-phase, it is clear from the different responses of **G1-ene** and **G1-ane**, that the primary interaction between the alkene group and Ag^+ must lie at the heart of the sensory response.

To finally test the mechanism of cation-induced gel breakdown, we used ^{13}C NMR to monitor the samples. In the native gel of **G1-ene** in ethyl acetate, the resonances associated with the gelator are broadened as the gelator is immobilised within the gel fibres. When either $AgSbF_6$ or $LiPF_6$ was added to the gel, however, the sample showed ^{13}C NMR gelator peaks as the gelator became mobile (Fig. 6). Importantly, the resulting chemical shifts closely resemble the chemical shifts of **1-ene** when bound to either Ag^+ or Li^+—with the distinctive upfield shifts of the alkene ^{13}C resonances associated with the formation of Ag^+–alkene interactions being clearly observed. This proves the cations complex to **G1-ene** in the proposed manner, which leads to the gel–sol conversion.

In conclusion, this study has shown that the Ag^+–alkene interaction is essential for the response of **G1-ene** to $AgSbF_6$. This is demonstrated by **G1-ane**, which is unable to respond to Ag^+ but still able to respond to Li^+. There is no response of any of these gels to larger, less charge dense Group 1 metal ions such as Na^+ and K^+, and we propose that the selectivity amongst Group 1 metals is mediated by the higher charge density of Li^+, meaning it is a stronger binder to C═O than Na^+ or K^+. We suggest that the response to Ag^+ seen in gels of **G1-ene** is caused by repulsive electrostatic repulsions between alkene-bound Ag^+ ions, although we cannot rule out the hypothesis that binding to the alkenes subsequently allows Ag^+ to interact better with the C═O groups within the gel fibres, hence disrupting them. In summary, this is the first example in which Ag^+–alkene interactions play a vital role in mediating a response in soft matter systems, providing fundamental insight into the nature of this interaction and acting as a step on the way to development of heavy-metal-responsive materials.

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Notes and references

1 (*a*) *Molecular Gels: Materials with Self-Assembled Fibrillar Networks*, ed. P. Terech and R. G. Weiss, Springer, Dordrecht, The Netherlands, 2006; (*b*) D. K. Smith, *Molecular Gels-Nanostructured Soft Materials in Organic Nanostructures*, ed. J. L. Atwood and J. W. Steed, Wiley-VCH, Weinheim, 2008; (*c*) J. W. Steed, *Chem. Commun*., 2011, **47**, 1379–1383.
2 (*a*) S. Banerjee, R. K. Das and U. Maitra, *J. Mater. Chem*., 2009, **19**, 6649–6687; (*b*) A. R. Hirst, B. Escuder, J. F. Miravet and D. K. Smith, *Angew. Chem., Int. Ed*., 2008, **47**, 8002–8018.
3 M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke and J. W. Steed, *Chem. Rev*., 2010, **110**, 1960–2004.
4 (*a*) H.-J. Kim, J.-H. Lee and M. Lee, *Angew. Chem., Int. Ed*., 2005, **44**, 5810–5814; (*b*) H.-J. Kim, W.-C. Zin and M. Lee, *J. Am. Chem. Soc*., 2004, **126**, 7009–7014; (*c*) Y. He, Z. Bian, C. Kang and L. Gao, *Chem. Commun*., 2011, **47**, 1589–1591; (*d*) Y. He, Z. Bian, C. Kang and L. Gao, *Chem. Commun*., 2010, **46**, 5695–5697; (*e*) S. Zhang, S. Yang, J. Lan, S. Yang and J. You, *Chem. Commun*., 2008, 6170–6172; (*f*) Q. Liu, Y. Wang, W. Li and L. Wu, *Langmuir*, 2007, **23**, 8217–8223; (*g*) L. Applegarth, N. Clarke, A. C. Richardson, A. D. M. Parker, I. Radosavljevic-Evans, A. E. Goeta, J. A. K. Howard and J. W. Steed, *Chem. Commun*., 2005, 5423–5425; (*h*) S. I. Kawano, N. Fujita, K. J. C. van Bommel and S. Shinkai, *Chem. Lett*., 2003, **32**, 12.
5 (*a*) D. Braga, S. d'Agostino, E. D'Amen and F. Grepioni, *Chem. Commun*., 2011, **47**, 5154–5156; (*b*) J. Dash, A. J. Patil, R. N. Das, F. L. Dowdall and S. Mann, *Soft Matter*, 2011, **7**, 8120–8126; (*c*) M. O. M. Piepenbrock, N. Clarke and J. W. Steed, *Soft Matter*, 2011, **7**, 2412–2418; (*d*) P. Casuso, P. Carrasco, I. Loinaz, H. J. Grande and I. Odriozola, *Org. Biomol. Chem*., 2010, **8**, 5455–5458; (*e*) K. Chen, L. Tang, Y. Xia and Y. Wang, *Langmuir*, 2008, **24**, 13838–13841.
6 (*a*) S. V. Brignell and D. K. Smith, *New J. Chem*., 2007, **31**, 1243–1249; (*b*) G. M. Dykes and D. K. Smith, *Tetrahedron*, 2003, **59**, 3999–4009; (*c*) K. Murata, M. Aoki, T. Nishi, A. Ikeda and S. Shinkai, *J. Chem. Soc., Chem. Commun*., 1991, 1715–1719.
7 W. Deng and D. H. Thompson, *Soft Matter*, 2010, **6**, 1884–1887.
8 (*a*) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc*., 1938, **60**, 836–847; (*b*) N. J. Barnett, L. V. Slipchenko and M. S. Gordon, *J. Phys. Chem.A*, 2009, **113**, 7474–7481.
9 J. Burgess and P. J. Steel, *Coord. Chem. Rev*., 2011, **255**, 2094–2103.
10 C. M. Wiliams and L. N. Mander, *Tetrahedron*, 2001, **57**, 425–447.
11 C. D. M. Beverwijk and J. P. C. M. van Dongen, *Tetrahedron Lett*., 1972, **13**, 4291–4294.
12 (*a*) J. R. Moffat, I. A Coates, F. J. Leng and D. K. Smith, *Langmuir*, 2009, **25**, 8786–8793; (*b*) J. R. Moffat and D. K. Smith, *Chem. Commun*., 2009, 316–318.
13 D. Stacchiola, G. Wu, M. Kaltchev and W. T. Tysoe, *Surf. Sci*., 2001, **486**, 9–23.
14 M. J. Hynes, *J. Chem. Soc., Dalton Trans*., 1993, 311–312.