

Self-recovering stimuli-responsive macrocycle-equipped supramolecular ionogels with unusual mechanical properties†

Cite this: *Org. Biomol. Chem.*, 2014, **12**, 503

Zhenhui Qi,^a Nora L. Traulsen,^a Paula Malo de Molina,^{‡b} Christoph Schlaich,^a Michael Gradzielski^{*b} and Christoph A. Schalley^{*a}

A chiral, crown-ether-functionalized bisurea gelator forms supramolecular gels in ionic liquids. The resulting ionogels show a remarkably high thermal stability with gel–sol transition temperatures (T_{gs}) reaching more than 100 °C. The mechanical strength of these ionogels is surprisingly high and even comparable to that of cross-linked protein fibres. Furthermore, the ionogels exhibit rapid self-recovery properties after structural damage caused by deformation. Pseudorotaxanes form from the gelators' benzo[21]-crown-7 ethers as the wheels and secondary ammonium ions as the axles despite the competition between that cation and the imidazolium ions of the ionic liquid for crown ether binding. Pseudorotaxane formation as an external chemical stimulus triggers the gel–sol transition of the ionogels.

Received 24th July 2013,
Accepted 19th November 2013

DOI: 10.1039/c3ob41523f

www.rsc.org/obc

Introduction

Low molecular weight gelators (LMWGs) represent an interesting type of soft materials which have received considerable attention due to their reversibility and often easy-to-control stimuli responsiveness.¹ Numerous responsive LMWGs have been applied in drug or protein delivery,² catalysis,³ self-recovering materials⁴ and many other applications.⁵ However, designing new types of LMWGs and predicting their gelation behaviour remain challenging. Earlier studies were often based on serendipitous discovery of new gelators or on the structural optimization of already known gelator lead structures.⁶

As the solvent has a major influence not only on the gelator's solubility, but also on the non-covalent interactions connecting the individual molecules to form a fibrous network, the environment has a major impact on gelation. Apart from the most frequently tested solvents such as water or the conventional organics, ionic liquids⁷ – although employed in many diverse

areas – have been only rarely used in gel chemistry. They have been widely recognized as a new generation of green solvents due to their unique physical properties, including negligible vapour pressure, high thermal stability, non-flammability, and exceptional electrochemical properties.⁸ These characteristics have endowed them with a broad range of applications in science, technology and industry, such as organic synthesis (*e.g.* solvents, catalysis), engineering (*e.g.* coatings, lubricants), electrochemical devices (*e.g.* electrolytes, solar cells) and biological use (*e.g.* as active pharmaceutical ingredients).⁹

Ionogels are gels that form in ionic liquids, which can for example be achieved by polymerization or classical sol–gel processes.¹⁰ They keep the main properties of ionic liquids, but prevent them from flowing, thus greatly expanding their scope of applications.¹¹ The investigation of LMWG-based ionogels began only recently,¹² compared to the tremendous progress made with the low-molecular-weight hydro- and organogelators.¹³ The LMWG-based ionogels reported so far have great potential in that they combine the advantages of ionic liquids with the particular mechanical properties of supramolecular gels.¹⁴ However, the stimuli responsiveness of the most known ionogels has so far been restricted to thermally reversible¹⁵ and photo-responsive ionogels.¹⁶ Also, the mechanical strengths of LMWG-based ionogels are usually far from that required for practical uses. From the point of view of material applications, it is challenging to integrate simple processability, stimuli-responsiveness and mechanical properties into a single ionogel.

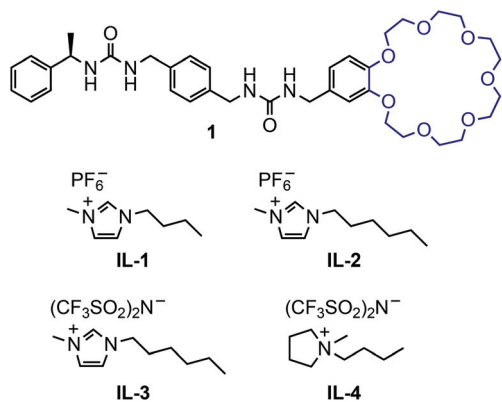
Recently, we designed and synthesized the benzo[21]crown-7-functionalized LMWG **1** (Scheme 1). It is based on a bisurea

^aInstitut für Chemie und Biochemie, Freie Universität Berlin, Takustrasse 3, 14195 Berlin, Germany. E-mail: christoph@schalley-lab.de; Fax: +49 30-838-55817; Tel: +49 30-838-52639

^bInstitut für Chemie, Sekretariat TC7, Technische Universität Berlin, Strasse des 17. Juni 124, 10623 Berlin, Germany. E-mail: michael.gradzielski@tu-berlin.de; Fax: +49 30 314 26602; Tel: +49 30 314 24934

† Electronic supplementary information (ESI) available: Additional experiments for the rheological characterization of the gels; experiments demonstrating the formation of pseudorotaxanes as a trigger for the sol–gel transition; ITC experiments supporting the stimuli-responsive behavior. See DOI: 10.1039/c3ob41523f

‡ Present address: Department of Chemical Engineering, University of California Santa Barbara, 3357 Engineering II, Santa Barbara, USA.



Scheme 1 Chemical structures of macrocycle-functionalized gelator **1** and the ionic liquids IL-1 to IL-4 under study here.

scaffold¹⁷ which exhibits quite impressive gelation abilities in a number of organic solvents, particularly in acetonitrile.¹⁸ Here, we report the finding that this crown-ether-functionalized chiral bisurea derivative forms ionogels with different ionic liquids and is thus the first macrocycle-functionalized gelator used in this context. Employing ionic liquids not only significantly increases the mechanical strength of the resulting gels to levels far beyond those observed in organic solvents such as acetonitrile, but also creates ionogels exhibiting unusually rapid self-recovering properties. Furthermore, the molecular recognition properties of the crown ether can be used to generate ionogels responsive to chemical stimuli.

Results and discussion

Gelation study

Several studies correlated the gelling power of LMWGs to the solvent polarity¹⁹ as expressed in Reichardt's $E_T(30)$ polarity scale.²⁰ We found that the E_T values for the organic solvents gelled by **1** range from 36.0 to 55.4 kcal mol⁻¹ (Fig. 1). This range also includes ionic liquids, *e.g.* IL-1 with its E_T value of 52.3 kcal mol⁻¹ that is more at the upper end of the E_T window of gelation.²¹ Therefore, we suspected our crown-equipped gelator to be able to form gels in ionic liquids.

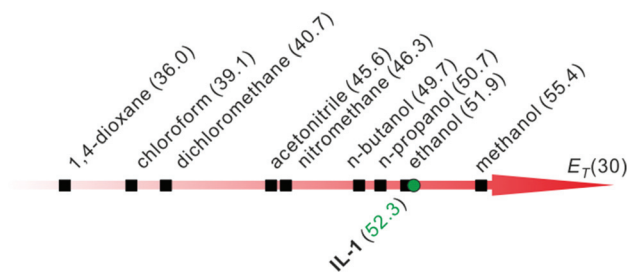


Fig. 1 The E_T polarity scale of the organic solvents in which **1** forms gels. The green spot indicates the $E_T(30)$ value of ionic liquid IL-1 which falls into the range of the more polar organic solvents gelled by **1**.

Table 1 Gelation ability of gelator **1** in selected ionic liquids

Entry	Ionic liquid	State	CGC
1	IL-1	Gel	1.14 wt% (23.0 mM)
2	IL-2	Gel	0.47 wt% (15.3 mM)
3	IL-3	Gel	1.48 wt% (31.2 mM)
4	IL-4	Gel	2.92 wt% (60.6 mM)

The gelation behaviour of **1** was evaluated in four different ionic liquids (Table 1). The critical gelation concentration (CGC) of **1** in IL-1, below which no gel forms, is 1.14 wt%. Qualitatively, gelation is also observed when the hexafluorophosphate counterion is replaced by triflimide (IL-2 *vs.* IL-3) or when the cation is changed to pyrrolidinium (IL-4). Quantitatively, the critical gelation concentrations differ somewhat depending on these changes. In IL-2, gelator **1** is most potent with a relatively low CGC of 0.47 wt%. This value is even comparable with many efficient polymeric gelators.²² In IL-4, which bears the pyrrolidinium cation, the gelator showed only a moderate gelation ability (CGC = 2.92 wt%).

Thermostability

All ionogels display thermal reversibility. They melt upon heating and turn back into a gel upon cooling. This indicates that the LMWGs self-assemble into the typical gel networks that were already observed for gelator **1** in organic solvents.¹⁸ A quite high thermostability of the ionogels is expressed in the gel-sol phase transition temperatures T_{gs} , which reach values significantly higher than 373 K at increased gelator concentrations (Fig. 2a). This thermal stability suggests that these ionogels can be used as quasi-solid ionic materials even at relatively high temperatures.

$$\ln X_g = -\frac{\Delta H_m}{RT_{gs}} + C \quad (1)$$

With the Schröder-van Laar equation (eqn (1)), the melting enthalpies ΔH_m can be calculated from the slope of a semi-logarithmic plot of $\ln X_g$ over T^{-1} (Fig. 2b).²³ X_g in this equation is the molar fraction of the gelator in the ionic liquid and ΔH_m the melting enthalpy of the gel. Quite substantial values are obtained, which are likely due to the strong cation-anion attraction in the ionic liquids.²⁴

FT-IR characterization and gel morphology

The urea functionality has been widely used in LMWGs, because it provides a convenient 1D directionality and strong intermolecular hydrogen-bonding interactions.²⁵ Therefore, Fourier-transform infrared (FT-IR) spectra were recorded to probe the hydrogen bonding in the ionogels. As summarized in Table 2, all ionogels exhibit similar N-H stretch bands ranging from 3316 to 3329 cm⁻¹ and amide-I bands around 1616 cm⁻¹, indicating the existence of rather strong intermolecular hydrogen bonding between the urea groups even in the ionic liquid.²⁶ This is in agreement with earlier studies of this

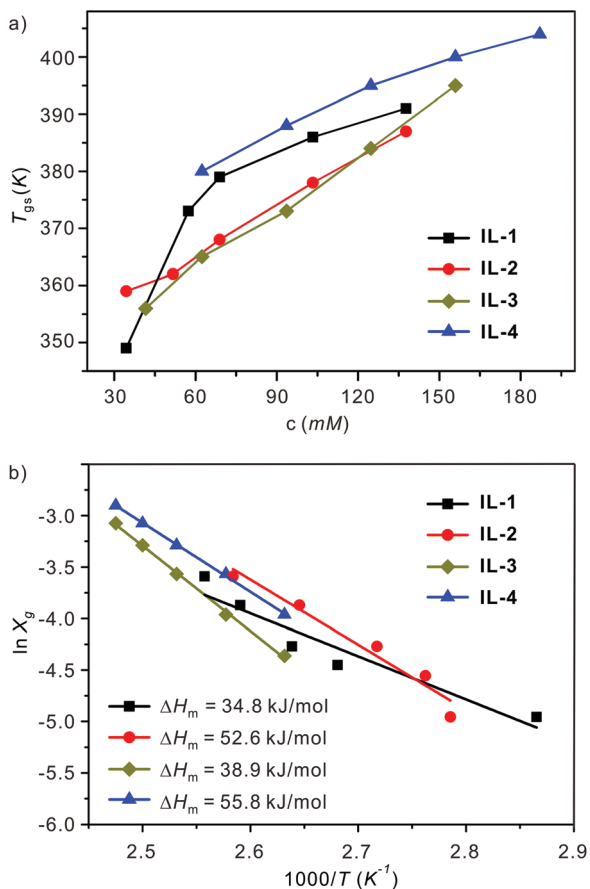


Fig. 2 (a) Variation of the gel-sol transition temperature T_{gs} with the gelator concentrations of the ionogels. (b) Semi-log plot of $\ln X_g$ over $1/T$ for the four ionogels to evaluate the melting enthalpies according to the Schröder-van Laar equation.

Table 2 FT-IR data for gels of **1** in different solvents^a

Solvents	Absorptions/cm ⁻¹		
	NH-stretch	Amide-I	Amide-II
IL-1	3316.0	1616.1	1582.1
IL-2	3326.6	1616.1	1560.1
IL-3	3319.9	1617.0	1568.8
IL-4	3329.5	1615.1	1571.7
CH ₃ CN	3325.5	1611.1	1568.6

^aAll spectra are recorded at room temperature using the spectrum of the pure ionic liquid as the background for subtraction.

gelator in acetonitrile and other organic solvents that showed that PF₆⁻ does not interfere with these hydrogen bonding interactions.^{1f,18}

Unlike gels in conventional solvents, direct observation of the morphology of the ionogels by electron microscopy or atomic force microscopy is not straightforward, due to the high boiling points of the ionic liquids. So far, the morphologies of ionogels as reported by others have been determined after a careful exchange of the ionic liquid by suitable organic solvents.^{10a,12} Previously, atomic force microscopy

(AFM) was performed on gels of both enantiomers of **1** in acetonitrile and this resulted in images showing numerous entangled fibres forming cavities in which the solvent is trapped. According to the presence of analogous strong hydrogen bonding, we infer from the previous studies that such fibrous network structures are present also in the ionogels under study.

Rheological characterization and SANS and SAXS experiments

The mechanical properties of the ionogels and the reversibility of their changes are two of the most important factors to be considered for practical and sustainable applications. Therefore, all ionogels were examined using a Malvern (Bohlin) Gemini rheometer employing a plate-plate geometry at a constant temperature of 25 °C (for details see ESI†). In order to determine the range of linear viscoelastic behaviour, we performed strain-amplitude sweeps on the gel samples. All ionogels studied exhibit elastic responses. The storage moduli G' decrease rapidly above critical strains of 0.5–1%, indicating a strain-induced collapse of the gel state (Fig. 3a) and the corresponding nonlinear viscous behaviour in that range. The critical strain of the tested ionogels does not depend much on the type of ionic liquid, and varies only slightly from one to another. Accordingly, the oscillatory shear experiments were done for a fixed deformation of 0.5%. The obtained storage

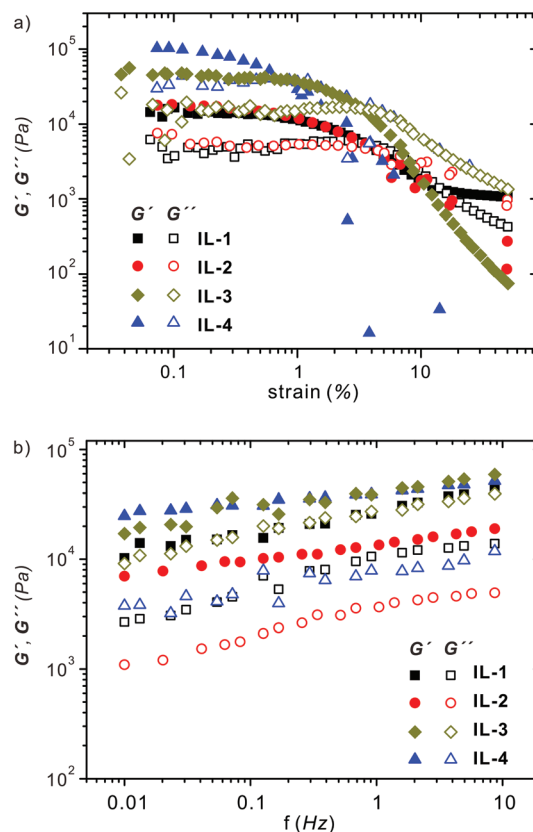


Fig. 3 Oscillatory rheological analysis of the ionogels (30 mM for IL-1 and IL-2, 60 mM for IL-3 and IL-4): (a) storage and loss moduli G' and G'' obtained from a strain-amplitude sweep performed at 10 Hz. (b) Storage and loss moduli obtained from a frequency sweep performed at 0.5% strain.

moduli G' and loss moduli G'' of all the gel samples are plotted against the frequency (Fig. 3b), and G' was constantly greater than G'' for the entire range of frequencies. This shows that all the gels are dominated by their elastic properties, show the typical behaviour of a Bingham fluid²⁷ and possess a yield stress (in our case of 6–60 Pa for the different ILs), which is usually observed for gel materials.²⁸

$$G' \approx G^0 = {}^1NkT \quad (2)$$

Interestingly, the mechanical strength of the ionogels is significantly higher than that of gels of **1** in conventional organic solvents (Fig. 4). The gel in acetonitrile exhibits a moderate mechanical strength with a storage modulus G' reaching 2000 Pa at a concentration of 40 mM (3.6 wt%).¹⁰ In marked contrast, G' of the ionogel of **1** in **IL-1** reaches a 15-fold higher value of 30 000 Pa already at a concentration of 30 mM (1.5 wt%). These values are substantially higher than those of physically cross-linked networks formed from F-actin filaments (10–500 Pa)²⁹ or other associated polymers, but less than those of collagen (~1 GPa) or gelatin (~1 MPa). The value of G' further increased with an increase in the concentration of **1** and eventually reached 1.6×10^5 Pa at 60 mM (3 wt%, Fig. 4 and ESI, Fig. S1†). This value is exceptionally high and comparable with the G' values of hydrogels based on cross-linked protein fibres³⁰ as well as ionogels based on polymeric gelators,¹⁴ but here achieved by a process of self-assembly. Consequently, network formation in ionic liquids **IL-1** to **IL-4** is more effective than that in acetonitrile. From the storage moduli, one can estimate an effective number density 1N of elastic network points of one network point per $(3.3\text{--}6.5 \text{ nm})^3$ based on a simple network theory described by eqn (2).³¹ This is a remarkably high effective cross-linking density and can be considered as the rheologically relevant structural size of the elastic network. It is interesting to note that for the highest gelator concentration of 60 mM the concentration of effective network points becomes 48 mM, *i.e.*, here basically every gelator molecule stores about one kT elastic energy, this again showing the high elastic efficacy of this network. **IL-1**, however, appears to be particularly good for forming a network: the mechanical strength of the other ionogels is still

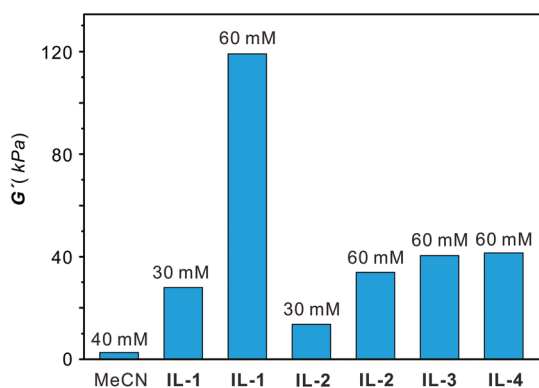


Fig. 4 Storage moduli G' of gels of **1** in different solvents. All data have been obtained under the same conditions (1 Hz and 0.5% strain).

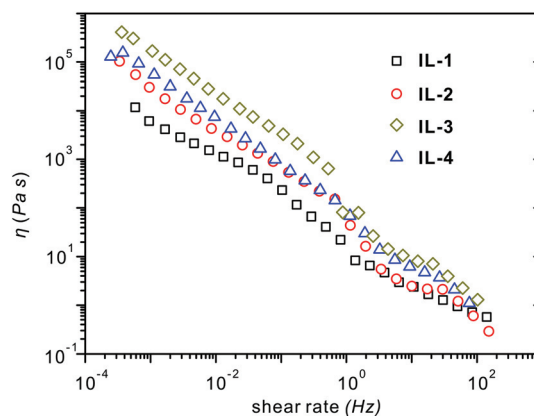


Fig. 5 Viscosity as a function of the shear rate for ionogels **1** in different ionic liquids (30 mM for **IL-1** and **IL-2**, 60 mM for **IL-3** and **IL-4**). Each point was measured after 150 seconds shearing.

significantly higher than those of the gel in acetonitrile, but much lower than that of the ionogel in **IL-1**.

In steady-shear measurements, a typical shear thinning for LMWGs is observed (Fig. 5). The viscosity dramatically decreases ($\eta = 10^5 \text{ Pa s} \rightarrow 10^0 \text{ Pa s}$) when the shear rate increases ($\dot{\gamma} = 10^{-4} \text{ s}^{-1} \rightarrow 10^2 \text{ s}^{-1}$), *i.e.*, one has a scaling law $\eta \sim \dot{\gamma}^{-0.9}$. Shear-thinning is characteristic of gels non-covalently assembled from LMWGs and is caused by the disruption of the non-covalent interactions and thus the fibre network at sufficiently high shear rates.

Intriguingly, the ionogel of **1** in **IL-1** exhibits a rapid recovery with a characteristic time of 150 s of its high viscosity after a breakdown induced by applying higher shear rates (Fig. 6). The complete recovery was fully reproducible for at least eight cycles. To the best of our knowledge, this is the first observation of such a rapid recovery in an LMWG-based ionogel, although a similarly rapid recovery has been previously reported in several polymer based systems and in self-assembling surfactant systems.³² We suggest that the rapid recovery is primarily caused by a shear-induced disruption of gel domains rather than disturbances of the local gel network.

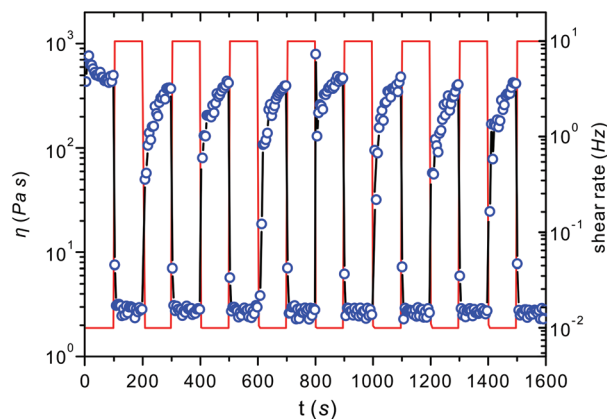


Fig. 6 Step-rate time-sweep measurements displaying recovery of the 30 mM ionogel of **1** in **IL-1**. Blue circles represent the shear viscosity and the red line the applied shear rate.

Similar arguments have been put forward for other rapidly recovering gels.³³

To obtain further insight into the structural organization of the ionogels, small-angle X-ray and neutron scattering (SAXS, SANS) experiments were performed on **IL-1** (30 mM). However, due to the rather low contrast of the gelator and the ionic liquid, these experiments remained rather inconclusive with respect to the detailed structure. SAXS shows a q^{-2} dependence for the higher q -range of 0.1–1 nm⁻¹ (ESI, Fig. S5†), which is rather unspecific, but could be interpreted such that the structural correlation length is of the order of ~20 nm (see ESI† for details). At lower q ($q < 0.1$ nm⁻¹) the SANS experiments show a steeper increase with a $q^{-3.65}$ dependence (ESI, Fig. S6†). Despite the fact that our SAXS and SANS data are quite noisy (due to the generally poor contrast) such a behaviour is in good agreement with observations on polymer hydrogels³⁴ and one may assume that our ionogels are structurally similar to such systems. In addition, the lack of peaks or pronounced scattering features shows that there are no more highly ordered structures in the size range of 2–100 nm.

Gel–sol transitions induced by molecular recognition

Most studies devoted to the effects of ionic liquids on the molecular recognition behaviour of supramolecules have been conducted in mixed solvent systems so far, while studies in pure ionic liquids are quite rare.³⁵ Benzo[21]crown-7 (**BC7**) is the smallest crown ether capable of forming pseudorotaxane structures with alkyl-substituted secondary ammonium ions (Scheme 2).³⁶ This recognition motif has been applied in the construction of elaborate supramolecular architectures.³⁷ However, the formation of pseudorotaxane structures in pure ionic liquids has not been investigated so far. Gelator **1** is equipped with **BC7** so that the gel–sol transitions might be triggered by pseudorotaxane formation upon addition of monovalent guest **G1** to the gel.

Before studying the stimulus-responsive behaviour of the gel, first the host–guest properties of **G1** and **BC7** in ionic liquids were examined. Isothermal titration calorimetry (ITC) is a powerful technique for measuring the thermodynamics and stoichiometry in solution.³⁸ ITC measurements using **BC7** and **G1** in the four ionic liquids resulted in the binding data summarized in Table 3. The binding isotherms fit nicely to a 1:1 binding model (ESI, Fig. S6†), which is consistent with pseudorotaxane formation. The binding constants K_a of **BC7** and **G1** in the four ionic liquids range from 350 M⁻¹ to

Table 3 Thermodynamic data for the host–guest binding of **BC7** and **G1** in different ionic liquids

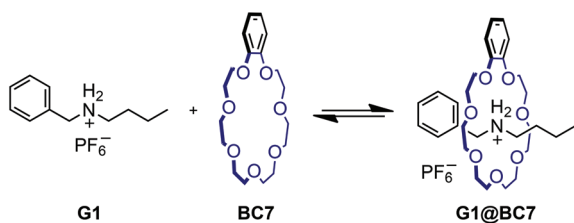
	K_a (M ⁻¹)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	$-T\Delta S$ (kJ mol ⁻¹)
IL-1	550	-15.6	-21.9	6.3
IL-2	350	-14.5	-21.6	7.1
IL-3	970	-17.0	-18.4	1.4
IL-4	5300	-21.2	-31.9	10.7

5300 M⁻¹. For the imidazolium-cation-based ionic liquids, all K_a values are below 1000 M⁻¹ and close to those measured for the same host–guest complex in acetone (615 M⁻¹).²⁶ In **IL-4**, the K_a value turns out to be significantly higher with 5300 M⁻¹. This indicates the nature of the cation to play a pivotal role, while the anion has only minor effects on pseudorotaxane formation. All cations can interact with the crown ether oxygen atoms through C–H...O hydrogen bonds with their polarized methyl and methylene groups. In addition, the electron deficient aromatic ring of the imidazolium cation can form π -donor– π -acceptor interactions with the electron-rich benzene ring of the crown ether. Competition between the aromatic imidazolium cations and **G1** is thus more pronounced than that between the pyrrolidinium cation and **G1**. Overall, however, the formation of pseudorotaxanes is possible in the tested ionic liquids. It should thus be possible to trigger gel–sol transitions of the ionogels under study by applying **G1** as the external chemical stimulus.

Indeed, the addition of three equivalents of **G1** is sufficient to trigger the gel–sol transitions (Fig. 7a) in all four ionogels. The gel–sol transitions can be reversed by triethylamine (TEA) addition. Deprotonation of the secondary ammonium ion causes dethreading and the gel regenerates. In order to demonstrate pseudorotaxane formation to be the reason for the gel–sol transition, dibenzylammonium hexafluorophosphate has been used as a control. As the benzyl groups are sterically too demanding to thread through the crown ether, one would expect no gel–sol transition to occur as a pseudorotaxane cannot form. This is indeed the case (Fig. 7b), so that we can safely conclude pseudorotaxane formation to be the reason for the gel–sol transition rather than a disruption of the urea–urea hydrogen bonding by the PF₆⁻ anions.

Conclusions

Gelator **1** is the first macrocycle-functionalized gelator for ionic liquids. It forms ionogels in a variety of ionic liquids, which combine very high thermal stability with gel–sol transition temperatures above 100 °C with a surprising mechanical strength as expressed in storage moduli much higher than those determined for gels of the same gelator in typical organic solvents. Thus, a very effective gel network is formed. The storage moduli of the ionogels are even comparable with those measured for gels containing cross-linked protein fibres. Moreover, the ionogels under study revealed a rapid recovery after applying mechanical stress that disrupts the gel network,



Scheme 2 The formation of pseudorotaxane structure based on **BC7** and its secondary ammonium guest **G1**.

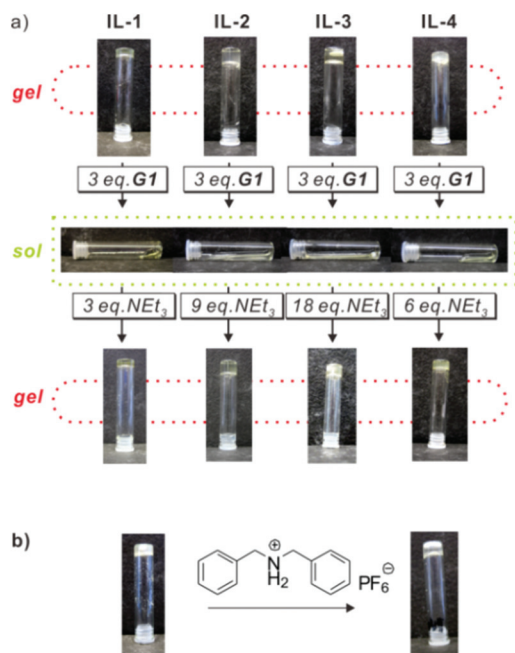


Fig. 7 (a) Ionogels prepared from the four ionic liquids (top) and their stimuli-responsive behaviour: gel–sol transitions can be triggered by the formation of pseudorotaxanes with **G1**. Deprotonation of **G1** results in dethreading and the ionogel re-forms. (b) Control experiment performed with the ionogel of **1** in IL-1: when dibenzyl ammonium hexafluorophosphate is added, which is unable to thread through the crown ether, the gel remains stable.

an aspect that is due to the fact that the gel network is formed by a reversible process of self-assembly. Finally, the ionogels are stimuli-responsive: the crown ether can be utilized as a recognition unit for secondary ammonium ions that form pseudorotaxanes and thus trigger the gel–sol transition. By deprotonation and dethreading of the ammonium ion, the gel can be regenerated. To the best of our knowledge, gelator **1** is the first low-molecular-weight gelator that is addressable by external chemical stimuli.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 765 and SCHA 893/5-3) for financial support. Z. Q. is grateful to the China Scholarship Council (CSC) for a Ph.D. fellowship. For help with the rheological measurements, we would like to thank Benjamin von Lospichl. For the SAXS and SANS experiments we acknowledge substantial support by Sylvain Prévost.

Notes and references

- (a) P. Terech and R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133; (b) L. A. Estroff and A. D. Hamilton, *Chem. Rev.*, 2004, **104**, 1201; (c) N. M. Sangeetha and U. Maitra, *Chem. Soc. Rev.*, 2005, **34**, 821; (d) A. R. Hirst, B. Escuder, J. F. Miravet and D. K. Smith, *Angew. Chem., Int. Ed.*, 2008, **47**, 8002; (e) S. Banerjee, R. K. Das and U. Maitra, *J. Mater. Chem.*, 2009, **19**, 6649; (f) E. A. Appel, J. del Barrio, X. J. Loh and O. A. Scherman, *Chem. Soc. Rev.*, 2012, **41**, 6195; (g) L. E. Buerkle and S. J. Rowan, *Chem. Soc. Rev.*, 2012, **41**, 6089; (h) A. Noro, M. Hayashi and Y. Matsushita, *Soft Matter*, 2012, **8**, 6416; (i) Z. Qi, P. Malo de Molina, W. Jiang, Q. Wang, K. Nowosinski, A. Schulz, M. Gradzielski and C. A. Schalley, *Chem. Sci.*, 2012, **3**, 2073.
- (a) F. Zhao, M. L. Ma and B. Xu, *Chem. Soc. Rev.*, 2009, **38**, 883; (b) A. Friggeri, B. L. Feringa and J. van Esch, *J. Controlled Release*, 2004, **97**, 241; (c) J. J. Panda, A. Mishra, A. Basu and V. S. Chauhan, *Biomacromolecules*, 2008, **9**, 2244; (d) P. K. Vemula, G. A. Cruikshank, J. M. Karp and G. John, *Biomaterials*, 2009, **30**, 383.
- (a) B. Escuder, F. Rodriguez-Llansola and J. F. Miravet, *New J. Chem.*, 2010, **34**, 1044; (b) D. Diaz Diaz, D. Kuhbeck and R. J. Koopmans, *Chem. Soc. Rev.*, 2011, **40**, 427.
- (a) M. Zhang, D. Xu, X. Yan, J. Chen, S. Dong, B. Zheng and F. Huang, *Angew. Chem., Int. Ed.*, 2012, **51**, 7011; (b) X. Yan, D. Xu, J. Chen, M. Zhang, B. Hu, Y. Yu and F. Huang, *Polym. Chem.*, 2013, **4**, 3312.
- (a) T. Kato, Y. Hirai, S. Nakaso and M. Moriyama, *Chem. Soc. Rev.*, 2007, **36**, 1857; (b) S. S. Babu, S. Prasanthkumar and A. Ajayaghosh, *Angew. Chem., Int. Ed.*, 2012, **51**, 1766.
- (a) P. Dastidar, *Chem. Soc. Rev.*, 2008, **37**, 2699; (b) J. H. van Esch, *Langmuir*, 2009, **25**, 8392.
- (a) P. Walden, *Bull. Acad. Imp. Sci.*, 1914, **8**, 405; (b) P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772; (c) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (d) J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508; (e) S. T. Handy, *Curr. Org. Chem.*, 2005, **9**, 959; (f) S. Werner, M. Haumann and P. Wasserscheid, *Annu. Rev. Chem. Biomol. Eng.*, 2010, **1**, 203; (g) O. Zech and W. Kunz, *Soft Matter*, 2011, **7**, 5502.
- (a) R. D. Rogers and K. R. Seddon, *Science*, 2003, **302**, 792; (b) M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621; (c) J. Dupont, *Acc. Chem. Res.*, 2011, **44**, 1223.
- (a) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (b) N. V. Plechkova and K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123; (c) J. W. Lee, J. Y. Shin, Y. S. Chun, H. B. Jang, C. E. Song and S.-g. Lee, *Acc. Chem. Res.*, 2010, **43**, 985; (d) T. Torimoto, T. Tsuda, K.-i. Okazaki and S. Kuwabata, *Adv. Mater.*, 2010, **22**, 1196; (e) C. Maton, N. De Vos and C. V. Stevens, *Chem. Soc. Rev.*, 2013, **42**, 5963.
- (a) T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii and T. Aida, *Science*, 2003, **300**, 2072; (b) P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar and M. Grätzel, *J. Am. Chem. Soc.*, 2003, **125**, 1166; (c) M. P. Scott, M. Rahman and C. S. Brazel, *Eur. Polym. J.*, 2003, **39**, 1947; (d) P. Snedden, A. I. Cooper, K. Scott and N. Winterton, *Macromolecules*, 2003, **36**, 4549; (e) M. A. B. H. Susan, T. Kaneko, A. Noda and M. Watanabe, *J. Am. Chem. Soc.*, 2005, **127**, 4976; (f) Z. Li, H. Liu, Y. Liu, P. He, J. Li, L. Zheng and J. Li, *Polymer*, 2005, **46**, 7578; (g) H. Nakajima and H. Ohno, *Polymer*, 2005, **46**, 11499;

- (h) T. Kato, A. Okazaki and S. Hayase, *Chem. Commun.*, 2005, 363; (i) T. Fukushima and T. Aida, *Chem.-Eur. J.*, 2007, **13**, 5048; (j) M.-A. Néouze, J. Le Bideau, P. Gaveau, S. Bellayer and A. Vioux, *Chem. Mater.*, 2006, **18**, 3931; (k) S. Shimano, H. Zhou and I. Honma, *Chem. Mater.*, 2007, **19**, 5216; (l) K. Ueno, K. Hata, T. Katakabe, M. Kondoh and M. Watanabe, *J. Phys. Chem. B*, 2008, **112**, 9013; (m) J. Wang, H. Chu and Y. Li, *ACS Nano*, 2008, **2**, 2540; (n) J. Lu, F. Yan and J. Texter, *Prog. Polym. Sci.*, 2009, **34**, 431; (o) J. Zhang, Q. Zhang, X. Li, S. Liu, Y. Ma, F. Shi and Y. Deng, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1971; (p) A. Vioux, L. Viau, S. Volland and J. Le Bideau, *C. R. Chim.*, 2010, **13**, 242.
- 11 J. Le Bideau, L. Viau and A. Vioux, *Chem. Soc. Rev.*, 2011, **40**, 907.
- 12 (a) N. Kimizuka and T. Nakashima, *Langmuir*, 2001, **17**, 6759; (b) N. Mohmeyer, D. Kuang, P. Wang, H.-W. Schmidt, S. M. Zakeeruddin and M. Gratzel, *J. Mater. Chem.*, 2006, **16**, 2978; (c) G. Feng, Y. Xiong, H. Wang and Y. Yang, *Electrochim. Acta*, 2008, **53**, 8253; (d) T. Tu, X. Bao, W. Assenmacher, H. Peterlik, J. Daniels and K. H. Dötz, *Chem.-Eur. J.*, 2009, **15**, 1853; (e) S. Dutta, D. Das, A. Dasgupta and P. K. Das, *Chem.-Eur. J.*, 2010, **16**, 1493; (f) A. K. Gupta, M. P. Singh, R. K. Singh and S. Chandra, *Dalton Trans.*, 2012, **41**, 6263; (g) S. K. Mandal, T. Kar, D. Das and P. K. Das, *Chem. Commun.*, 2012, **48**, 1814; (h) N. Minakuchi, K. Hoe, D. Yamaki, S. Ten-no, K. Nakashima, M. Goto, M. Mizuhata and T. Maruyama, *Langmuir*, 2012, **28**, 9259; (i) S. S. Moganty, S. Srivastava, Y. Lu, J. L. Schaefer, S. A. Rizvi and L. A. Archer, *Chem. Mater.*, 2012, **24**, 1386; (j) J. C. Ribot, C. Guerrero-Sanchez, T. L. Greaves, D. F. Kennedy, R. Hoogenboom and U. S. Schubert, *Soft Matter*, 2012, **8**, 1025; (k) J. Yan, J. Liu, P. Jing, C. Xu, J. Wu, D. Gao and Y. Fang, *Soft Matter*, 2012, **8**, 11697.
- 13 (a) M. George and R. T. Weiss, *Acc. Chem. Res.*, 2006, **39**, 489; (b) J. H. v. Esch and B. L. Feringa, *Gels in Encyclopedia of Supramolecular Chemistry*, Taylor & Francis, 2007, p. 586.
- 14 (a) K. Hanabusa, H. Fukui, M. Suzuki and H. Shirai, *Langmuir*, 2005, **21**, 10383; (b) W. Kubo, S. Kambe, S. Nakade, T. Kitamura, K. Hanabusa, Y. Wada and S. Yanagida, *J. Phys. Chem. B*, 2003, **107**, 4374; (c) A. Ikeda, K. Sonoda, M. Ayabe, S. Tamaru, T. Nakashima, N. Kimizuka and S. Shinkai, *Chem. Lett.*, 2001, 1154; (d) N. Kimizuka and T. Nakashima, *Langmuir*, 2001, **17**, 6759; (e) M. Amai, H. Kobayashi and S. Shinkai, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 2553; (f) K. Hanabusa, K. Hiratsuka, M. Kimura and H. Shirai, *Chem. Mater.*, 1999, **11**, 649.
- 15 K. Hanabusa, H. Fukui, M. Suzuki and H. Shirai, *Langmuir*, 2005, **21**, 10383.
- 16 (a) F. Benito-Lopez, R. Byrne, A. M. Raduta, N. E. Vrana, G. McGuinness and D. Diamond, *Lab Chip*, 2010, **10**, 195; (b) A. Kavanagh, R. Byrne, D. Diamond and K. J. Fraser, *Membranes*, 2012, **2**, 16.
- 17 (a) J. van Esch, S. De Feyter, R. M. Kellogg, F. De Schryver and B. L. Feringa, *Chem.-Eur. J.*, 1997, **3**, 1238; (b) F. S. Schoonbeek, J. H. van Esch, R. Hulst, R. M. Kellogg and B. L. Feringa, *Chem.-Eur. J.*, 2000, **6**, 2633; (c) Y. Jeong, K. Hanabusa, H. Masunaga, I. Akiba, K. Miyoshi, S. Sakurai and K. Sakurai, *Langmuir*, 2005, **21**, 586; (d) C. Wang, D. Zhang and D. Zhu, *Langmuir*, 2006, **23**, 1478.
- 18 Z. Qi, C. Wu, P. Malo de Molina, H. Sun, A. Schulz, C. Griesinger, M. Gradzielski, R. Haag, M. B. Ansorge-Schumacher and C. A. Schalley, *Chem.-Eur. J.*, 2013, **19**, 10150.
- 19 A. R. Hirst and D. K. Smith, *Langmuir*, 2004, **20**, 10851.
- 20 C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319.
- 21 S. Zhang, N. Sun, X. He, X. Lu and X. Zhang, *J. Phys. Chem. Ref. Data*, 2006, **35**, 1475.
- 22 J. i. Nagasawa, H. Matsumoto and M. Yoshida, *ACS Macro Lett.*, 2012, **1**, 1108.
- 23 J. Weiss, M. Koepf and J. A. Wytko, in *Self-Assembly of Supramolecular Wires in Supramolecular Chemistry: From Molecules to Nanomaterials*, ed. P. Gale and J. Steed, Wiley, 2012.
- 24 H. Sato, T. Yajima and A. Yamagishi, *Chem. Commun.*, 2011, **47**, 3736.
- 25 J. W. Steed, *Chem. Soc. Rev.*, 2010, **39**, 3686.
- 26 R. M. Versteegen, R. P. Sijbesma and E. W. Meijer, *Macromolecules*, 2005, **38**, 3176.
- 27 (a) E. C. Bingham, *Fluidity and Plasticity*, McGraw-Hill, New York, 1922; (b) J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1980.
- 28 (a) P. L. Luisi, R. Scartazzini, G. Haering and P. Schurtenberger, *Colloid Polym. Sci.*, 1990, **268**, 356; (b) C. M. Garner, P. Terech, J.-J. Allegraud, B. Mistrot, P. Nguyen, A. de Geyer and D. Rivera, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2173; (c) P. Terech, D. Pasquier, V. Bordas and C. Rossat, *Langmuir*, 2000, **16**, 4485; (d) M. Burkhardt, S. Kinzel and M. Gradzielski, *J. Colloid Interface Sci.*, 2009, **331**, 514.
- 29 J. H. Shin, M. L. Gardel, L. Mahadevan, P. Matsudaira and D. A. Weitz, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 9636.
- 30 A. A. Martens, J. van der Gucht, G. Eggink, F. A. de Wolf and M. A. Cohen Stuart, *Soft Matter*, 2009, **5**, 4191.
- 31 P. J. Flory, *J. Chem. Phys.*, 1950, **18**, 108.
- 32 E. A. Appel, X. J. Loh, S. T. Jones, F. Biedermann, C. A. Dreiss and O. A. Scherman, *J. Am. Chem. Soc.*, 2012, **134**, 11767.
- 33 (a) T. J. Deming, *Soft Matter*, 2005, **1**, 28; (b) P. Cordier, F. Tournilhac, C. Soulie-Ziakovic and L. Leibler, *Nature*, 2008, **451**, 977.
- 34 (a) F. Horkay, W. Burchard, A.-M. Hecht and E. Geissler, *Macromolecules*, 1993, **26**, 1296; (b) F. Horkay, P. J. Basser, A.-M. Hecht and E. Geissler, *Polymer*, 2005, **46**, 4242.
- 35 X. H. Shen, Q. D. Chen, J. J. Zhang and P. Fu, in *Supramolecular Structures in the Presence of Ionic Liquids in Ionic Liquids: Theory, Properties, New Approaches*, ed. A. Kokorin, InTech, Rijeka, Croatia, 2011.
- 36 (a) C. Zhang, S. Li, J. Zhang, K. Zhu, N. Li and F. Huang, *Org. Lett.*, 2007, **9**, 5553; (b) C. Zhang, K. Zhu, S. Li, J. Zhang, F. Wang, M. Liu, N. Li and F. Huang, *Tetrahedron Lett.*, 2008, **49**, 6917; (c) X. Yan, M. Zhou, J. Chen, X. Chi,

- S. Dong, M. Zhang, X. Ding, Y. Yu, S. Shao and F. Huang, *Chem. Commun.*, 2011, **47**, 7086.
- 37 (a) W. Jiang, H. D. F. Winkler and C. A. Schalley, *J. Am. Chem. Soc.*, 2008, **130**, 13852; (b) W. Jiang and C. A. Schalley, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 10425; (c) W. Jiang, A. Schäfer, P. C. Mohr and C. A. Schalley, *J. Am. Chem. Soc.*, 2010, **132**, 2309; (d) W. Jiang, D. Sattler, K. Rissanen and C. A. Schalley, *Org. Lett.*, 2011, **13**, 4502.
- 38 (a) W. Jiang, K. Nowosinski, N. L. Löw, E. V. Dzyuba, F. Klautzsch, A. Schäfer, J. Huuskonen, K. Rissanen and C. A. Schalley, *J. Am. Chem. Soc.*, 2012, **134**, 1860; (b) N. L. Löw, E. V. Dzyuba, B. Brusilowskij, L. Kaufmann, E. Franzmann, W. Maison, E. Brandt, D. Aicher, A. Wiehe and C. A. Schalley, *Beilstein J. Org. Chem.*, 2012, **8**, 234; (c) L. Kaufmann, E. V. Dzyuba, F. Malberg, N. L. Low, M. Groschke, B. Brusilowskij, J. Huuskonen, K. Rissanen, B. Kirchner and C. A. Schalley, *Org. Biomol. Chem.*, 2012, **10**, 5954.