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Supporting Information

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

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1. General methods

All reagents were commercially available and used as supplied without further purification, if not mentioned otherwise. Compounds **1**, **BC7**, and **G1** were synthesized by previously reported methods.[1] The four ionic liquids, i.e. 1-butyl-3-methylimidazolium hexafluorophosphate ([C4ImC1]PF_6, **IL-1**), 1-hexyl-3-methylimidazolium hexafluorophosphate ([C6ImC1]PF_6, **IL-2**), 1-hexyl-3-methylimidazolium bis(trifluormethylsulfonyl)imide ([C6ImC1]NTf_2, **IL-3**), and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C4PyC1]NTf_2, **IL-4**) were purchased from Sigma-Aldrich and used as obtained. FT-IR spectra were recorded on a Nicolet Avatar 320 FT-IR spectrometer.

Preparation of the ionogels: The gelator and solvents (CH_2Cl_2/ionic liquid, 1:5 (*v/v*)) were put into a capped test-tube and sonicated for 15 min to aid the dissolution process. Afterwards, the dichloromethane was removed in vacuo at room temperature. The sample vial was left standing for 12 h at ambient conditions. The gel state was evaluated by the stable-to-inversion-of-a-test-tube method. In the gel-sol transition tests, the sample vial was left for 15 min before the inversion test. The critical gelation concentration (cgc) is defined as the lowest concentration of the gelator which leads to a stable gel.

Gel-sol transition temperature measurements: T_{gs} was determined by a ‘dropping-ball method.[2] A small ball (166 mg) was placed on top of the gel in a test tube (inner diameter 1.0 cm), which was slowly heated in a oil bath at a rate of 1 K min^{-1}. T_{gs} is defined as the temperature, when the ball had reached the bottom of the test tube (the height of gel is 0.2 cm). Dropping-ball experiments were carried out at least in duplicate, and the T_{gs} obtained were reproducible to within ±2 ^{o}C. T_{gs} values were determined for several different gelator concentrations in order to evaluate the melting enthalpies according to the Schröder-van-Laar equation (see main text).

Guest-induced stimuli-responsive behavior: Guest **G1** was added to the test tube containing the already prepared gel. Subsequently, the capped test tube was heated, until the guest molecule was dissolved in the ionic liquid. The sample vial was left standing for 12 h at ambient conditions. The gel state was evaluated by the stable-to-inversion-of-a-test-tube method.

Rheological characterization of the gels: Rheology measurements were performed with a Malvern (Bohlin) Gemini 150 rheometer employing a plate-plate geometry (40 mm diameter; steel) with a gap of 400 micrometer and a constant temperature of 25 °C. Oscillatory measurements were performed at a fixed deformation of 0.005. The experiments were performed in the linear viscoelastic regime as ascertained by the amplitude sweeps performed at 1 and 10 Hz, and by confirming the sinusoidal shape of the response function during the measurements. The measurement range was from 0.01 - 10 Hz taking 50 measurement points spaced logarithmically. For the determination of the shear-rate-dependent viscosity, each gel was sheared for 150 s to ensure the steady-state shear viscosity to be measured. The regenerated ionogels after a guest-induced gel-sol/sol-gel transition cycle were left standing for 24 h at ambient conditions before rheological characterization.

Small-angle x-ray scattering (SAXS): SAXS measurements were performed on a SAXSess mc^2 instrument from Anton Paar. The X-ray beam of 1.542 Å wavelength was emitted by a sealed-tube Cu-Kα microsource. The sample was measured in a flow cell introduced into a temperature-controlled sample stage. The scattering pattern was recorded by a CCD detector and the data was analyzed with the SAXSquant software provided. The analysis process included a subtraction of the background, a desmearing of the curve by taking into account the beam profile, and a scaling by a calibration factor to obtain the absolute intensity.

Small-angle neutron scattering (SANS): SANS data were recorded on V4 at the Helmholtz-Zentrum-Berlin, Berlin, Germany. Three configurations were used, with sample-detector distances of 1.6, 6, and 15.9 m at wavelengths lambda of 0.46, 0.46 and 0.79 nm, respectively, thus covering a q-range of 0.01 - 3.5 1/nm, where q is the magnitude of the wavevector ($q = (4\pi/\lambda)\cdot\sin(\theta/2)$, θ being the scattering angle). Samples were placed in sandwich cells with quartz windows, with a separation of 0.5 mm. Data reduction was performed with BerSANS,[3] using the scattering by H_2O 1 mm as a flat file at 1.6 and 6 m, and subtracting the scattering of the empty cell. The absolute scale was obtained from the calibrated level of water at 1.6 and 6 m, and from the direct beam flux at 15.9 m.

Isothermal titration calorimetry: ITC experiments were performed at 298 K in ionic liquids (**IL-1** to **IL-4**) on a TAM III (Waters GmbH, TA Instruments, Eschborn, Germany). In a typical titration experiment, a solution of **BC7** (800 µL, 1 mM) was placed in the sample cell. A solution of **G1** (250 µL, 10 mM) was placed in an injection syringe and was added stepwise. The titration schedule consisted of 25 consecutive injections with a 20 - 25 min interval in between. Heats of dilution were measured by blank titrations. The obtained data were analyzed with the instruments internal software package and were fitted with a 1:1 binding model.

2. Rheological characterization of the pristine ionogels

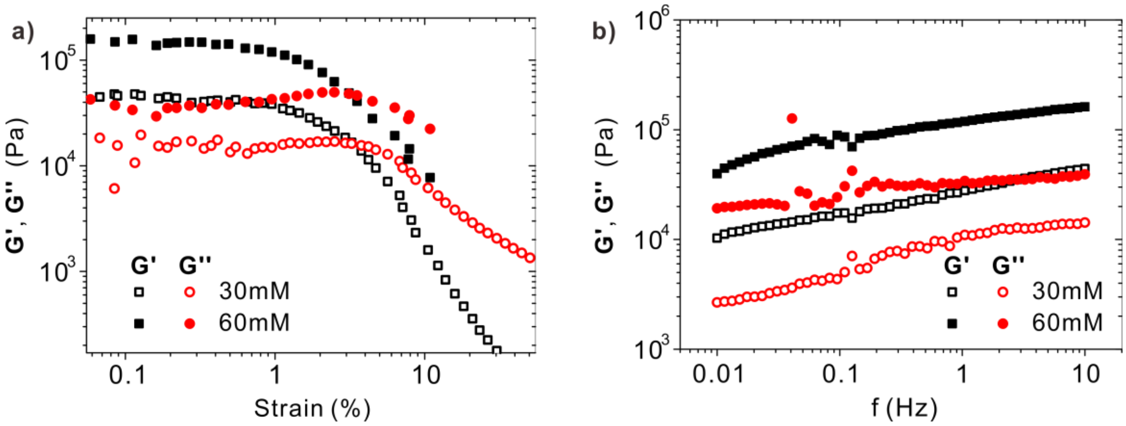

Figure S1. Concentration-dependent oscillatory measurements of the ionogel of **1** in **IL-1**: Storage and loss moduli obtained from a) a strain-amplitude sweep performed at 10 Hz and b) a frequency sweep performed at 0.5% strain.

3. Rheological characterization of ionogels recovered from a gel-sol transition

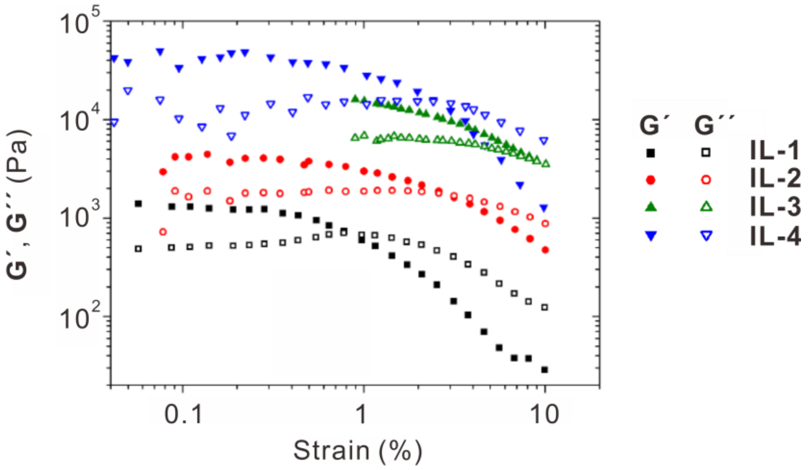

Figure S2. Storage and loss moduli obtained from a strain-amplitude sweep performed at 10 Hz of regained ionogels after a guest-induced gel-sol/sol-gel transition cycle.

A constant value of the moduli is observed up to a deformation of 0.01. For deformations higher than 0.01, a significant weakening of the gel properties is observed, indicating the network inside the ionogel to break. This behavior is similarly observed for the pristine gels (see above).

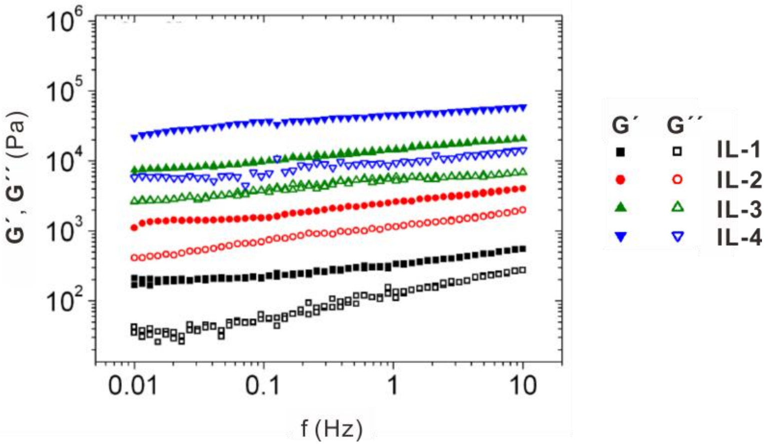

Figure S3. Storage and loss moduli obtained from a frequency sweep performed at 0.5% strain of ionogels regenerated after a gel-sol transition.

The data shows that the storage moduli G´ are still constantly greater than the loss moduli G´´ for the entire range of frequencies. The regenerated ionogels showed typical gel-like behavior. The G´ of regenerated ionogels after a gel-sol transition is still very high, indicating the high mechanical strength not to change significantly.

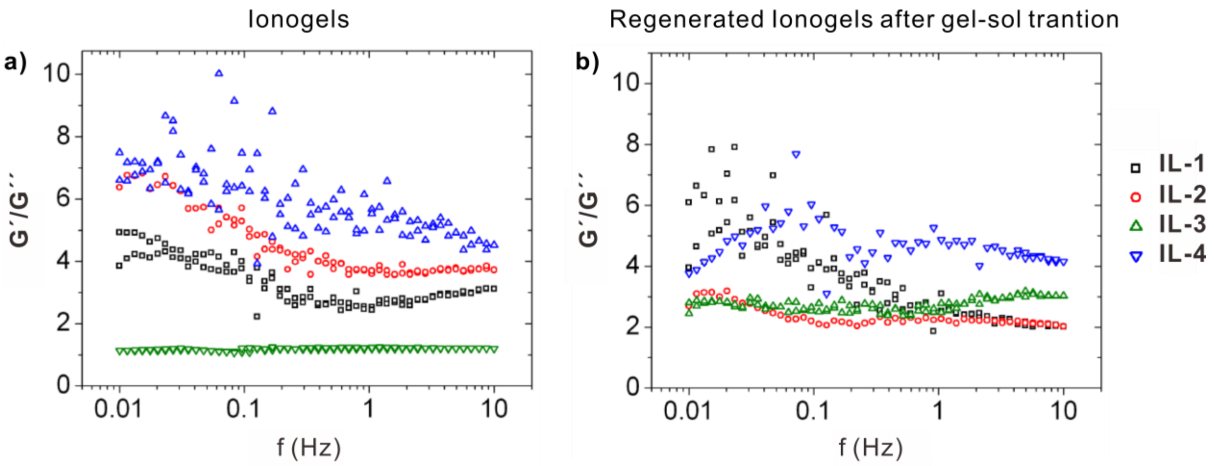

Figure S4. Ratio between the elastic and viscous moduli G'/G" of ionogels before and after the guest-induced gel-sol-gel transition cycle.

The ratio G´/G´´ is a measure of the relative elasticity of the gels compared to its viscous properties. The similarity of the values obtained for all the ionogels before and after gel-sol transition clearly indicates the elasticity not to be significantly changed after the reversible gel-sol transition.

4. SAXS and SANS experiments

The SAXS measurements depicted in Figure S5 clearly demonstrate a q^{-2} scaling behaviour of the intensity. However, such a scaling law is not very indicative for a particular sample structure, as it may be observed for a large variety of structures, such as flat extended systems (e. g. membranes), Gaussian polymer coils, or an Ornstein-Zernike behaviour. If one assumes the latter, the scattering would be described by:

$$I(q) = \frac{I(0)}{1 + q^2 \cdot \xi^2} \tag{S1}$$

where q is the magnitude of the scattering vector:

$$q = \frac{4\pi}{\lambda} \cdot \sin(\theta / 2) \tag{S2}$$

with θ being the scattering angle and λ being the wavelength.

Applying this relation to our SAXS data shows that the correlation length ξ, that describes the structural size of the scattering units, will be at least 20 nm, but could be substantially larger as in the experimental no plateau value is achieved yet.

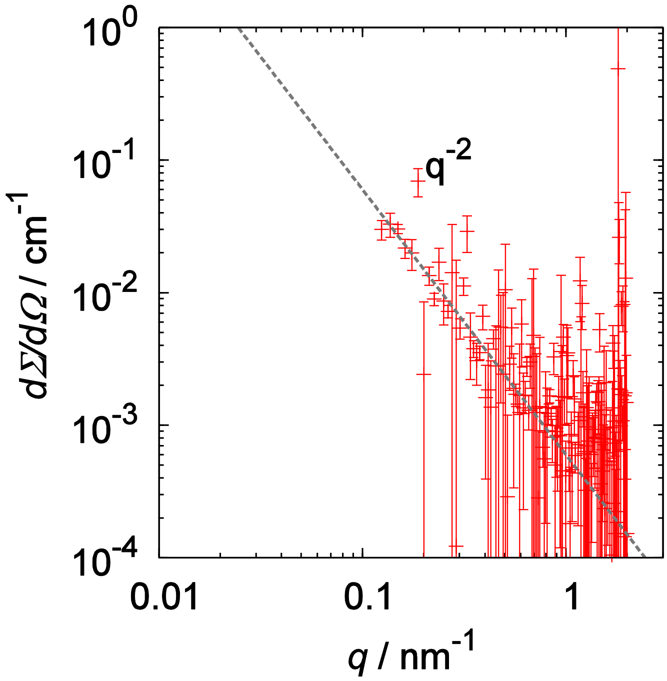

***Figure S5**. SAXS intensity as a function of the magnitude of the scattering vector for the ionogel of **1** in **IL-1** with a 30 mM concentration at 25 °C.*

As the SAXS data were not really conclusive we turned to do in addition SANS experiments as they allow in principle to go to much lower q. However from the molecular composition of the gelator and the ionic liquid it is also to be expected that the contrast is about a factor 10 less than in SAXS (scattering length density difference: SAXS: $2.38 \cdot 10^{-4}$ nm^{-2}; SANS: $0.23 \cdot 10^{-4}$ nm^{-2}). This is then seen in the rather low scattering intensity obtained in SANS (despite measuring times of up to one hour per configuration) and the scattering of the ionogel is almost identical to that of the ionic liquid without gelator (see Figure S6 left). After careful subtraction of the background and the scattering of the solvent one finds for the low q-range a power law behaviour of $q^{-3.65}$, as it is in a similar fashion often found for polymer gel networks. However, given the rather large subtracted background a rather high uncertainty remains with the precise scaling of the intensity. There is no good overlap between the SAXS and SANS data but again such a switch from a rather steep q-dependence ($q^{-3.65}$) to a much lower at higher q (q^{-2}) would again be in agreement with what otherwise has been observed for polymer hydrogels[4]. As the increase of the slope seen in SANS sets in just where the SAXS curve stops, the above estimated correlation length ξ of ~ 20 nm might be quite realistic.

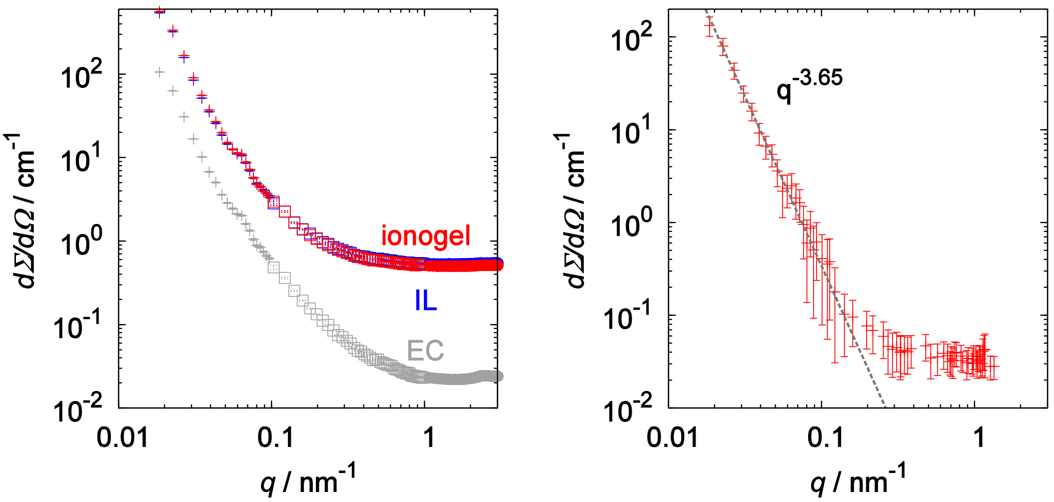

***Figure S6**. SANS intensity as a function of the magnitude of the scattering vector for the ionogel of **1** in **IL-1** with a 30 mM concentration at 25 °C. left: scattering intensity of empty cell (EC), ionic liquid (IL), and ionogel; right: scattering intensity of the ionogel after subtracting the background and the scattering of the ionic liquid.*

5. Control experiments on ionogels demonstrating formation of pseudorotaxanes as the trigger for the gel-sol transition

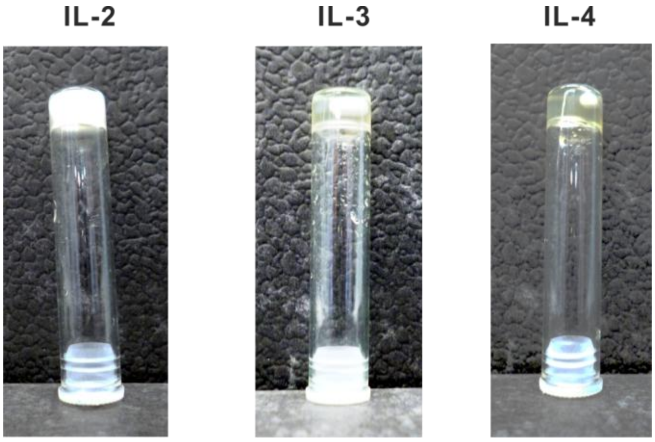

Figure S7. Ionogels obtained after the addition of 3.0 eq. dibenzylammonium hexafluorophosphate (30 mM for ionogel in **IL-2**, 60 mM for ionogels in **IL-3** and **IL-4**). Since the phenyl group is too large to penetrate the crown ether, no pseudorotaxanes form and the gels persist. The results of an analogous control experiment performed with **IL-1** are discussed in the main text.

6. Data obtained from ITC experiments.

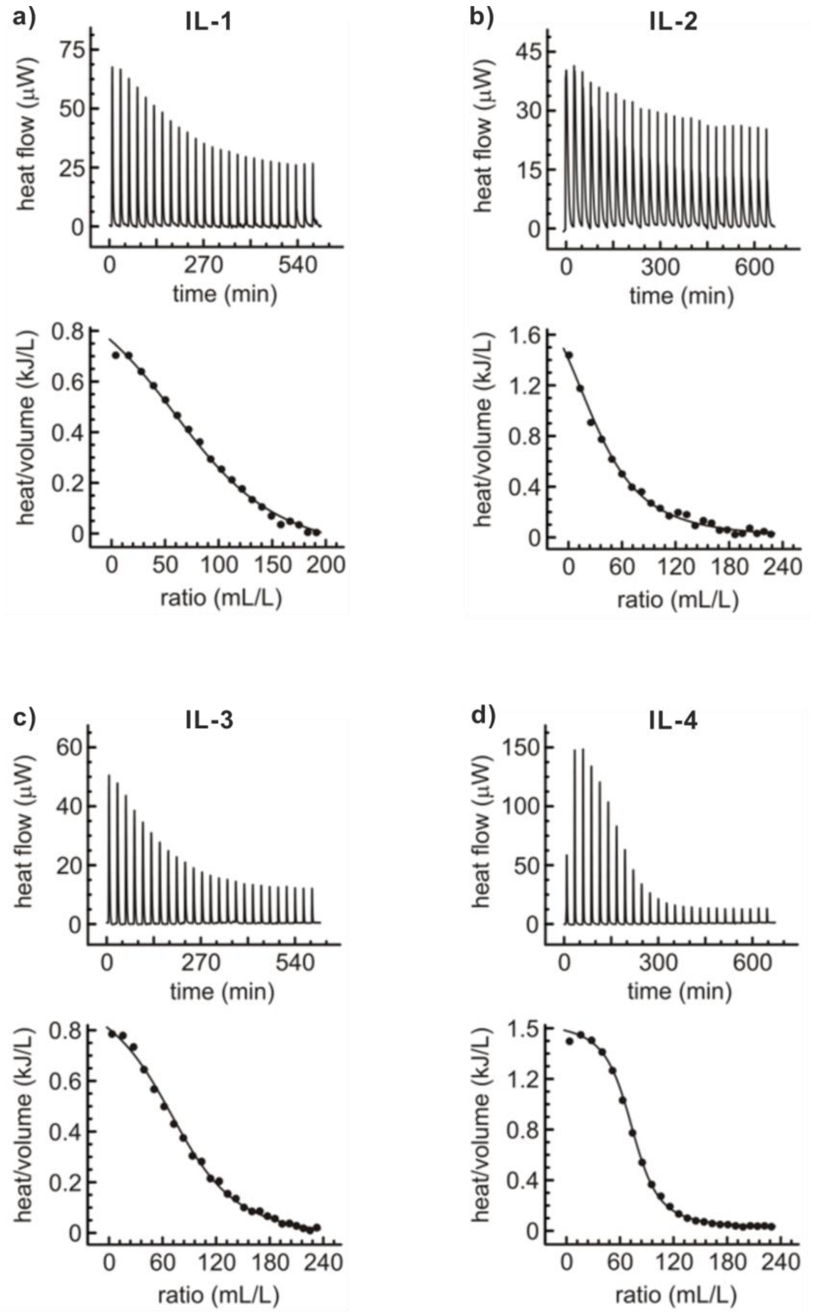

Figure S8. ITC titration experiments of **BC7** and guest **G1** in the four different ionic liquids.

7. References

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