LETTERS

High-water-content mouldable hydrogels by mixing clay and a dendritic molecular binder

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With the world's focus on reducing our dependency on fossil-fuel energy, the scientific community can investigate new plastic materials that are much less dependent on petroleum than are conventional plastics. Given increasing environmental issues, the idea of replacing plastics with water-based gels, so-called hydrogels, seems reasonable. Here we report that water and clay (2–3 per cent by mass), when mixed with a very small proportion (<0.4 per cent by mass) of organic components, quickly form a transparent hydrogel. This material can be moulded into shape-persistent, free-standing objects owing to its exceptionally great mechanical strength, and rapidly and completely self-heals when damaged. Furthermore, it preserves biologically active proteins for catalysis. So far[1] no other hydrogels, including conventional ones formed by mixing polymeric cations and anions[2,3] or polysaccharides and borax[4], have been reported to possess all these features. Notably, this material is formed only by non-covalent forces resulting from the specific design of a telechelic dendritic macromolecule with multiple adhesive termini for binding to clay.

Hydrogels can be prepared using a covalent or a non-covalent approach. Most polymer hydrogels, covalently crosslinked, are brittle, have poor transparency and lack the ability to self-heal[5]. Double-network hydrogels, an early example of synthetic polymer hydrogels, solved the problem of brittleness[6]. More recently, hybridization of polymers with clay nanosheets (CNSs) has been shown to give mechanically tough and transparent hydrogels[7–11]. However, the preparation of these materials uses *in situ* polymerization, which is lengthy and needs particular skills, and the products still lack the ability to self-heal.

We chose a non-covalent approach, owing to its advantages for easy, quick and reproducible preparation and the potential self-healing capability of the products[12]. Our material consists of four components: water, CNSs, a dendritic macromolecule (G*n*-binder; *n*, generation number; Fig. 1) and sodium polyacrylate (ASAP). Clay is a naturally occurring inorganic mineral salt with a layered structure, and is cheap to purchase[13]. On mixing with ASAP in water, CNSs, which are highly entangled with one another (Fig. 2a), are exfoliated and dispersed homogenously owing to the mutual repulsion caused by a possible site-specific wrapping of their positive-charged edge parts[13] with anionic ASAP (Fig. 2b). G*n*-binder possesses two dendron units[14], which are decorated with multiple guanidinium ion pendants on their peripheries (Fig. 1). A recently developed monodendron version of G*n*-binder, referred to as 'molecular glue', can be used for non-covalent functionalization of proteins by means of salt-bridge formation between the guanidinium ion pendants and oxyanionic surface groups of proteins[15]. In the course of the above study, we noticed that this dendron strongly adheres to the surface of glass. This observation motivated us to crosslink CNSs with G*n*-binder (Fig. 2c), as the nanosheet surfaces are full of oxyanions[13]. Because G*n*-binder carries adhesive dendron units at both termini of a long, hydrophilic PEG spacer (number-average molecular weight, $M_n = 10{,}650\ g\ mol^{-1}$), we expected that the nanosheets could be bound together to form a 3D network in water (Fig. 2c).

As described in Methods Summary, the hydrogel can be prepared quickly (3 min) by adding a very small proportion of G3-binder (0.15%) to a stirred aqueous solution of CNSs (2.0%) pretreated with ASAP (0.06%) (charge ratio (expressed in terms of the molar concentrations of charged groups), [CNSs (negative)]/[G3-binder (positive)]/[ASAP (negative)] = 18.0/2.0/6.0 mM; Fig. 2a–h). The gel can also form without ASAP, but a decrease in mechanical strength results. Later addition of ASAP does not enhance the mechanical strength. Exfoliation and homogeneous dispersion of CNSs by ASAP, as visualized using cryogenic transmission electron microscopy (Fig. 2i, j), are essential for increasing the CNS effective surface area for binding with G3-binder. Although guanidine hydrochloride, used in place of G*n*-binder under conditions identical to the above ([guanidinium ion] = 2.0 mM), caused no gelation, G2- and even G1-binder induced hydrogelation. Also important is the telechelic structure of G*n*-binder, as a monodendron version of G3-binder (PEG-G3-dendron; Fig. 1) did not cause gelation of water but precipitation of CNSs.

In Fig. 3a, the respective storage moduli, G', and loss moduli, G'', are shown for G*n*-binders ($n = 1$–3; [guanidinium ion] = 0.5 mM) as functions of angular frequency at a fixed strain, $\gamma = 1.0\%$. All three samples have a single plateau region in their dynamic moduli. The G' values have a substantial elastic response and are always larger than the G'' values over the entire range of frequencies. Among the three binders, G3-binder gives a hydrogel with the greatest G' value, suggesting a multivalent effect, as discussed previously for covalently crosslinked hydrogels[16,17]. As shown in Fig. 3c, the G' values depend on the amount of CNS. For example, by using 5.0% CNS in conjunction with 0.38% G3-binder and 0.15% ASAP, a G' value of 0.5 MPa was achieved, which is the largest among those reported for supramolecular hydrogels[1]. Although the systems without ASAP show the same trend in mechanical strength (Fig. 3b, d), pretreatment of CNSs with ASAP causes the G' value to increase by a factor of up to six.

As shown in Supplementary Fig. 1 (2.0% CNS, 0.15% G3-binder, 0.06% ASAP), the hydrogelation also takes place on heating but occurs more slowly as the temperature increases. Nevertheless, the mechanical properties of the hydrogels once formed hardly depend on the temperature (Supplementary Figs 2 and 3). At temperatures of $\geq 80\ ^{\circ}C$, bubbles of water vapour are generated inside the hydrogel owing to a 'boiling-stone' effect of CNSs (Supplementary Fig. 4). The

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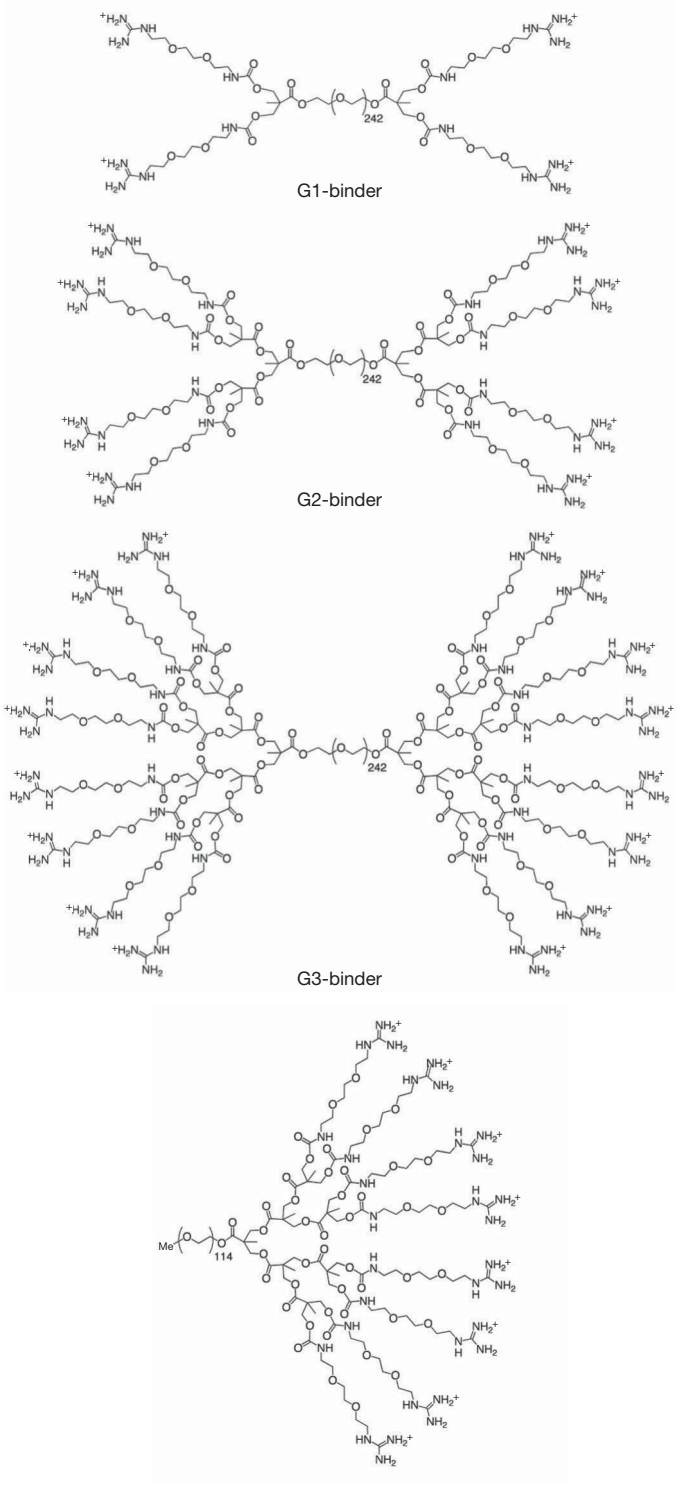

Figure 1 | Schematic structures of dendritic G*n*-binders (*n* = 1–3) and a monodendron analogue of G3-binder (PEG-G3-dendron). Owing to multivalency provided by the dendronized structure, the guanidinium ion groups strongly adhere to CNSs dispersed by sodium polyacrylate. G*n*-binders are telechelic and crosslink CNSs together to form a three-dimensional (3D) network in water. PEG, polyethylene glycol; Me, CH_3.

overall thermal properties of the hydrogel indicate that the hydrogelation takes place by kinetic trapping of the 3D network structure formed by the adhesion of G3-binder to CNSs. When the hydrogelation is conducted during heating, the dendritic branches of G3-binder may adopt a folded conformation as a result of dehydration, causing the 3D network to form slowly.

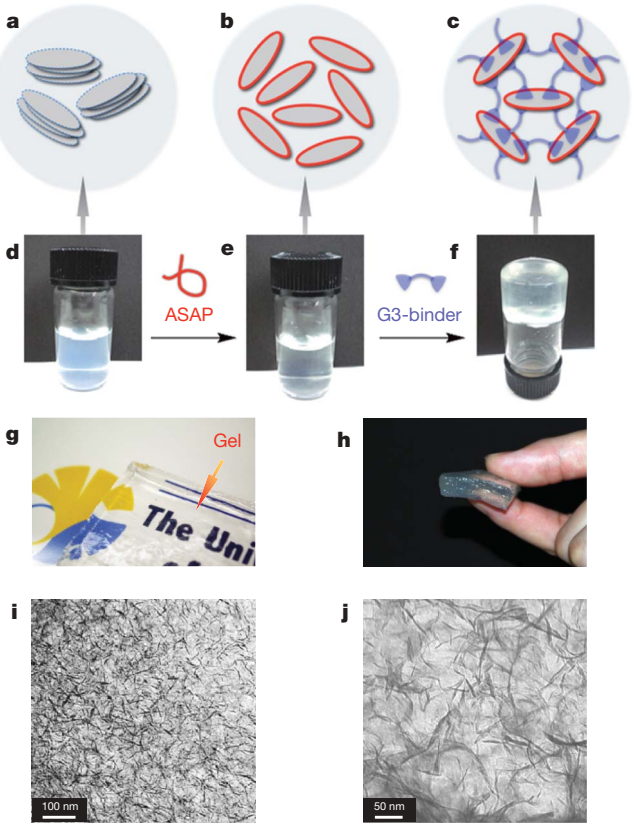

Figure 2 | Non-covalent preparation of hydrogels. **a–c**, Proposed mechanism for hydrogelation. CNSs, entangled with one another (**a**), are dispersed homogeneously by interaction of their positive-charged edge parts with anionic ASAP (**b**). Upon addition of G*n*-binder, exfoliated CNSs are crosslinked to develop a 3D network (**c**). **d–f**, Optical images of an aqueous suspension of CNSs (**d**), an aqueous dispersion of CNSs and ASAP (**e**) and a physical gel upon addition of G3-binder to the dispersion (**f**). **g**, **h**, The gel is transparent (**g**) and free standing (**h**). **i**, **j**, Cryogenic transmission electron microscopy micrographs of the hydrogel, showing homogeneously dispersed CNSs on different scales.

As shown in Fig. 3e, strain amplitude sweeps of the samples demonstrated an elastic response typical of hydrogels. The G' value of the toughest material, which contained 5.0% CNS, 0.38% G3-binder and 0.15% ASAP, rapidly decreases above the critical strain region ($\gamma = 9.0\%$), indicating a collapse of the gel state to a quasi-liquid state. We note that this sample exhibits very rapid recovery of its mechanical properties after a large-amplitude oscillatory breakdown, known as thixotropy (Fig. 3f). Under the application of a large-amplitude oscillatory force ($\gamma = 100\%$; frequency, $\omega = 6.0\ \mathrm{rad\ s^{-1}}$ (1.0 Hz)), the G' value decreases from 0.5 MPa to 5 KPa, resulting in a quasi-liquid state ($\tan\delta \equiv G''/G' \approx 3.0$–$4.0$). However, when the amplitude is decreased ($\gamma = 0.1\%$) at the same frequency (1.0 Hz), G' immediately recovers its initial value and the system returns to a quasi-solid state ($\tan\delta \approx 0.4$–0.5). The gel without ASAP is not free-standing. Accordingly, the yield stress, estimated from the oscillatory shear stress applied at the starting point of the decay of the storage modulus (G') in the strain-sweep profile, is less than 100 Pa, which is much smaller than that of the hydrogel with ASAP (>5,000 Pa).

Copolypeptide hydrogels[18], which were early examples of self-healing hydrogels, are mechanically much weaker (G' values <1 KPa) and, after a shear force is applied, require more than 1 h for G' to recover its initial value. Although oligomeric electrolyte hydrogels[19] have the ability to recover with a speed comparable to that of our hydrogel, their G' values are estimated to be 50 times smaller. Our hydrogel has both a large mechanical strength and a fast-recovery capability. The first feature may result largely from the mechanical toughness of CNSs, the main component of the 3D network in our material. Furthermore, the network

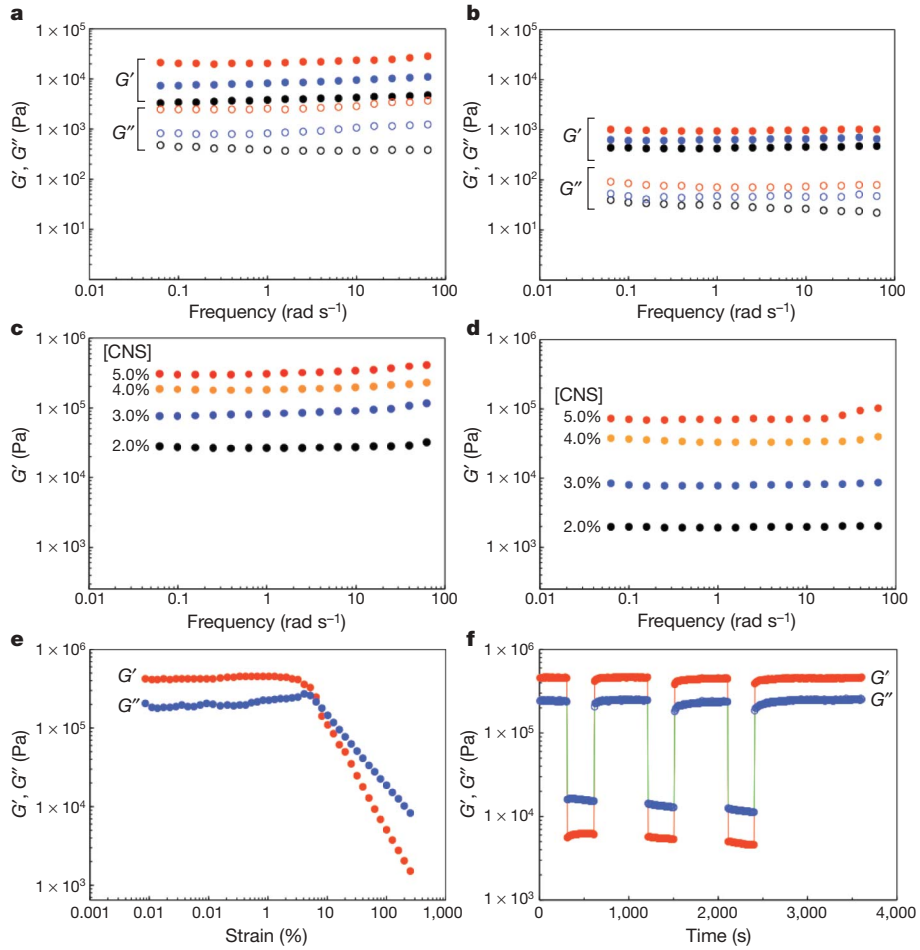

Figure 3 | Rheological properties (20 °C) of hydrogels. **a**, **b**, G' and G'' values of hydrogels (2.0% CNS, G*n*-binder ($n = 1$ (black), $n = 2$ (blue), $n = 3$ (red))) for [guanidinium ion] = 0.5 mM with (**a**) and without (**b**) 0.06% ASAP, on frequency sweep (from 0.06 to 60 rad s^{-1}). **c**, **d**, G' values of hydrogels (2.0–5.0% CNS, G3-binder) at weight ratios CNS/G3-binder/ASAP of 1.0/0.075/0.03 (**c**) and 1.0/0.075/0 (**d**), on frequency sweep (from 0.06 to 60 rad s^{-1}). **e**, **f**, G' and G'' values of a hydrogel (5.0% CNS, 0.38% G3-binder, 0.15% ASAP) on strain sweep (**e**) and in continuous step strain measurements (**f**).

structure is formed simply by attaching the guanidinium ion pendants of G*n*-binder to the exfoliated CNS surfaces, so the recovery process does not involve reassembly of organic components and is therefore quick.

Freshly cut surfaces of our hydrogels adhere to each other. As shown in Fig. 4a, we constructed a 3.5-cm-long bridge by connecting seven blocks. First two building blocks, both composed of 96.7% water, 3.0% CNS, 0.21% G3-binder and 0.09% ASAP, were sliced with a razor to expose fresh surfaces. Then the blocks were pushed together so that these surfaces came into contact with each other. New blocks were sliced and added in the same way until the bridge spanned a desired length. The resulting bridge is strong enough to hold when suspended horizontally, between two posts (Fig. 4a), or vertically, from a needle (Fig. 4b). If the blocks are not cut to obtain fresh surfaces, the fusion does not take place. Moreover, if the blocks are cut but left for more than a minute alone, they do not adhere to each other. We found that the freshly cut surfaces, essential for the adhesion of the blocks, are hydrophilic, as a deposited water droplet spread over a cut surface immediately but remained beaded on an uncut surface (Supplementary Fig. 5).

Unlike other supramolecular hydrogels, our material remains shape persistent even when immersed in an organic solvent such as tetrahydrofuran (THF). For example, a heart-shaped object (3.0 g), moulded using 97.8% water, 2.0% CNS, 0.14% G3-binder and 0.06% ASAP (Fig. 4c), was immersed in THF (9.0 g) for 6 h. When this procedure was repeated twice, the water in the moulded object, as determined by gas chromatography, was replaced with THF almost

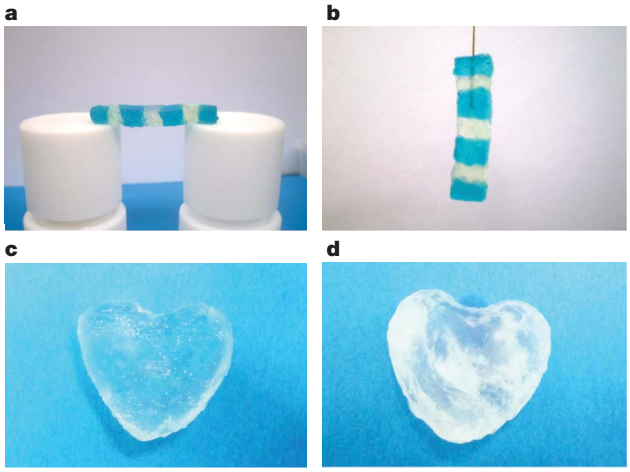

Figure 4 | Shape-persistent, free-standing macroscopic objects moulded from a hydrogel. Hydrogels with and without 0.01% methylene blue (for visibility) were prepared using 3.0% CNS, 0.21% G3-binder and 0.09% ASAP, and cut into small blocks. **a**, **b**, A bridge constructed by connecting together seven hydrogel blocks can be suspended horizontally (**a**) and held vertically (**b**). Diffusion of methylene blue from one block to the other hardly takes place, probably because of its adhesion to the CNS surfaces. **c**, **d**, Pictures of a heart-shaped hydrogel object before (**c**) and after (**d**) being immersed for 6 h three times in fresh THF at 20 °C.

completely. However, the gel network, even after the complete exchange of water for THF, maintained its form and integrity (Fig. 4d). Such an organogel cannot be formed directly from THF, CNSs and G*n*-binder, regardless of the presence of ASAP.

Whereas the preparation of most hydrogels generally relies on repeated heating/cooling cycles[20–24], ultrasonication[25], *in situ* polymerizations[6–11,26] or crosslinking reactions[27], our hydrogel can readily be prepared by mixing the three components in water at room temperature. We also found that the hydrogel lasts for a long time in salty water and also under moderately acidic or basic conditions (pH 4.0–10.0; Supplementary Fig. 6). Importantly for applications, even brine can be gelated by the addition of CNSs, G3-binder and ASAP, and G' remains almost unchanged, relative to the salt-free value, for [NaCl] = 0–10 mM (Supplementary Fig. 7). Because it is composed mostly of water, our self-standing hydrogel, although much tougher than other supramolecular hydrogels used for immobilizing enzymes[28–30], could incorporate and maintain biologically active proteins. As the first step towards this goal, we prepared a myoglobin-containing hydrogel by mixing CNSs (2.0%), G3-binder (0.04%) and ASAP (0.06%) in an aqueous solution of myoglobin (5.0 μM; Supplementary Fig. 8). No denaturation of the myoglobin was observed for at least one week, judging from its absorption spectral feature. Myoglobin is known to catalyse oxidation of *o*-phenylenediamine with H_2O_2. To investigate whether our tough hydrogel can provide a proper environment for catalysis, the myoglobin-containing hydrogel was added at 20 °C to a phosphate buffer solution of a mixture of *o*-phenylenediamine and H_2O_2. As shown in Fig. 5, myoglobin in the hydrogel retains an activity of ~71% relative to free myoglobin, despite the fact that G3-binder alone considerably reduces the activity (to 35%), probably by adhesion to the protein[15]. Thus, our shape-persistent hydrogel can transport biological activities.

Our material is not only environmentally friendly, readily prepared and self-healing (because it is non-covalent), but is also mouldable into various free-standing shapes owing to its large mechanical strength. Furthermore, simple moulded objects can be fused together to construct more complex architectures. By connecting together several blocks with different enzymatic activities, a certain reaction sequence might be designed. Our hydrogel contradicts the preconception that materials held together by supramolecular forces and mostly composed of water are weak, and may provide many interesting applications.

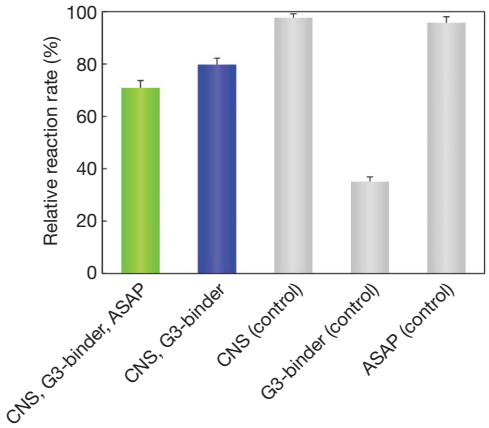

Figure 5 | Catalytic activities of myoglobin in hydrogels. Hydrogels were prepared by mixing 2.0% CNS with 0.04% G3-binder in a 5.0 μM aqueous solution of myoglobin with (green) and without (blue) 0.06% ASAP, and suspended in phosphate buffer (pH 7.4) containing *o*-phenylenediamine (10 mM). Then an aqueous solution of H_2O_2 was injected ([myoglobin]/[*o*-phenylenediamine]/[H_2O_2] = 0.5 μM/10 mM/25 mM), and a change in absorption at 420 nm due to 2,3-diamino-5,10-dihydrophenazine (product) was monitored at 20 °C. Error bars, s.d. ($N = 3$). All controls (grey) were measured under identical conditions. In every case, the reaction displayed a zero-order kinetics (linear correlation coefficient, $R > 0.99$).

METHODS SUMMARY

In a typical example of hydrogelation, we added 1.0 ml of an aqueous solution of ASAP (3.0 mg) at 20 °C to a stirred suspension of CNSs (100 mg) in water (3.75 ml). After 10 min, the suspension turned to a clear solution owing to exfoliation of CNSs (Fig. 2b, e). Then we added 0.25 ml of an aqueous solution of G3-binder (7.5 mg) dropwise while stirring. The mixture became completely stiff (Fig. 2c, f) within only 3 min, forming a transparent, self-standing material (Fig. 2g, h). We prepared other hydrogels similarly, but at different temperatures such as 10, 40, 50, 60, 70 and 80 °C (Supplementary Fig. 1). We measured rheological properties of the hydrogels (Fig. 3), including those prepared on heating (Supplementary Fig. 2), at 25 °C using a TA Instruments ARES-RFS controlled-strain rheometer, with a 25-mm-diameter para-plate attached to a transducer. The gap at the apex of the para-plate was set to be 0.5 mm. The samples were placed between the para-plate and the platform with special care to avoid evaporation of water. To investigate the recovery properties of the samples in response to applied shear forces, we used the following 1-h programmed procedure (applied shear force, expressed in terms of strain; duration in parentheses): 0.1% (300 s) → 100% (300 s) → 0.1% (600 s) → 100% (300 s) → 0.1% (600 s) → 100% (300 s) → 0.1% (1,200 s). We investigated temperature dependencies of the rheological properties of a hydrogel prepared at 20 °C, using a temperature-change programme: 25 °C → 10 °C → 70 °C → 25 °C, changing at a rate of 10 °C min^{-1} (Supplementary Fig. 3). The hydrogel prepared at 20 °C was heated to a designated temperature (60, 70 or 80 °C) for 10 min and cooled to 20 °C to investigate its macroscopic thermal stability (Supplementary Fig. 4).

Received 27 May; accepted 17 October 2009.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Acknowledgements Q.W. thanks the Japan Society for the Promotion of Science postdoctoral fellowship for foreign researchers. We thank Y. Arakawa for his support for the synthesis of PEG-G3-dendron.

Author Contributions Q.W. synthesized G*n*-binders and analysed the properties of hydrogels; K.O. and K.K. noticed adhesion of guanidinium-ion-appended dendrimers to glass surfaces; M.Y. assisted the rheological studies; E.L. and M.L. performed cryogenic transmission electron microscopy; and T.A., J.L.M. and Q.W. designed the study, analysed the data and wrote the paper.

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