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Self-healing and moldable material with deformation recovery ability from self-assembled supramolecular metallogels

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A self-assembled non-covalent metallogels system with self-healing, deformation recoverable, moldable and bottom-up load-bearing properties was prepared using tetrazolyl derivatives and Pd(OAc)$_2$.

10 Materials that are capable of autonomous healing upon damage are being developed rapidly due to their numerous potential applications (e.g. wound or fracture healing). [1] Over the past few decades, considerable efforts have been made to introduce covalently cross-linked polymers or supramolecular polymers 15 into the self-healable materials. [2, 3] However, an external trigger (energy or healing regents) is often required when a self-healing action is performed. Although significant progress has been made in polymers described above, the creation of self-healing materials by non-covalent interactions without "polymers" 20 continues to be a challenging and fascinating task. In this regard, self-assembled supramolecular gels are envisioned to be potential candidate for developing self-healing materials due to their superior reversibility of their formation and tunability compared to other polymeric gels. In spite of numerous reports have 25 elucidated the details of characterization and responsiveness of supramolecular gels[4], considerably less is known about their macroscopic self-healing behavior. [5-7]

Moldable materials that can form free-standing, shape-persistent objects are currently attracting much attention in soft 30 materials area. So far, most of the materials displaying both moldable and self-healing properties are a few hydrogels derived from polymers or a mixture of dendrimer and clay, [8, 9] and a limited number of supramolecular gels. [5, 6, 7c]

Herein we present a readily prepared self-healing and moldable 35 supramolecular metallogel system which stemmed from tetrazole-based ligands **1-4** (scheme 1) and Pd(OAc)$_2$. The tetrazole-based ligands feature easy preparation, achirality, and structural simplicity. To the best of our knowledge, **2** is the lowest molecular mass organic unit without any appending moieties that 40 participates in forming metallogel to date. A dimethylformamide (DMF) solution of **1-4** reacted with a DMF solution of Pd(OAc)$_2$ at a 2:1 molar ratio of tetrazolyl unit : Pd^{2+} at room temperature to spontaneously yield a complete and homogeneous gels (named gel **1-4**) with critical gel concentrations (CGC) were 3, 4.5, 3.6 45 and 3.9 % (w/v), respectively. [10] To explore the noncovalent interactions that actually influence the formation of the metallogel, the *NH* group of **1** were blocked by methyl groups to form the *N-Me* derivatives **5**. Remarkably, **5** was not capable of

evolving into any gel with Pd(OAc)$_2$ in the same condition. This 50 observation distinctly demonstrated that the cooperative hydrogen bonding interaction from the *NH* group of tetrazoles played a key role in the formation of gel (Fig. S1, ESI†). In this study, the gel **1** was chosen as a model system because of the relative low CGC comparing to other gels.
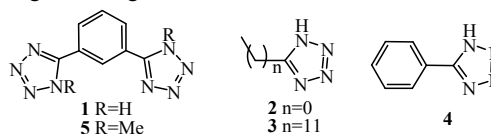
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Scheme 1 Chemical structures of ligands **1-5**

The AFM images clearly revealed that **1-4** and Pd(OAc)$_2$ spontaneously self-assembled into spherical particles with uniform shape and size. Taking gel **1** as an example, the average 60 diameter of the particles estimated from the size distribution after subtracting the tip-broadening parameters was 35.6 nm,[11] which is in good agreement with the TEM results. The dynamic light scattering (DLS) experiment of gel **1** also confirmed the formation of supermolecular aggregates in solution with an 65 average diameter about 30.5 nm. (Fig. S2, ESI†). Interestingly, the morphology evolution of gel **3** observed by TEM images provided considerable insight into the formation mechanism of a gel. Fig. 1a showed the dispersed spherical particles with a diameter of *ca*. 120-160 nm. However, as shown in Fig. 1b and 70 1c, more dense particles with a diameter of *ca*. 160-180 nm and interconnected bundles were unexpectedly observed on different matrixes of the same copper grid. We speculated that 1) the different density of particles might be attributed to the concentration difference as a result of the uneven dispersion of 75 the sample and 2) the strain release of spherical particles and surface defects likely accounts for the fusion of particles into thermodynamically more stable bundles. [12] Thus, it is reasonable to presume that the initially formed aggregates interconnected and further evolved into more dense and extended bundles, which 80 created an entangled network of that rigidified the solvent DMF.
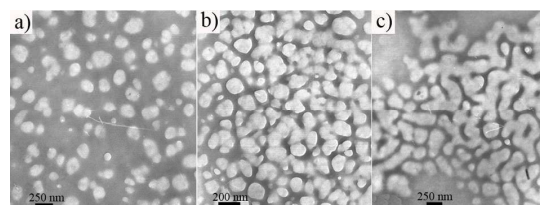
Fig. 1 (a-c) TEM images (unstained) of gel **3** on different matrixes on a carbon-coated copper grid from DMF (0.02 %).

The transparent gel **1** could be stable for more than one year at room temperature, and it could survive in a broad range of basic or acidic conditions (pH = 1-14). Moreover, the gel can tolerate heating (*ca.* 100 °C), shaking or sonication without any visible change or turning into a solution, which indicated the strong intermolecular interactions (e.g. coordination bonds, solvent-mediated hydrogen-bondings etc), stability and the coordination polymeric nature [13] of this supramolecular metallogel. The gel could be moulded into any self-supporting geometrical shape blocks, which demonstrated remarkable moldable and self-healing properties (Fig. 2). The block showed sticky instinct by adhering to a spatula or the bottom of a beaker (Fig. 2c and 2d). Interestingly, a gel sculpture (Fig. 2j) was taken out with care from a template after aging a solution of the gel **1** for several minutes, which depicts the head portrait of a girl. Thus, the gel could be fabricated into various geometric shapes using appropriate molds.
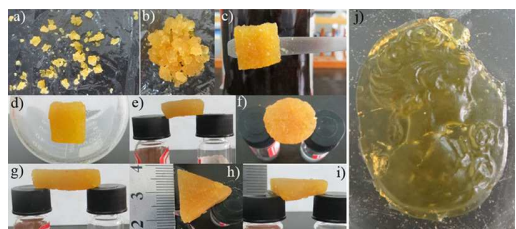
Fig. 2 (a-i) Shape-persistent, free-standing objects moulded from gel **1** (4 %), (j) a gel sculpture made from 4 % DMF solution of gel **1**.

Frequency sweep measurement displayed the storage modulus G′ approaches a plateau and are always greater than the loss modulus G″ over the entire range of frequencies, which implies that the substantial elastic response of the sample (Fig. S3a, ESI†). In addition, stress sweep measurements showed that both of the moduli are relatively constant, with G′ being typically an order of magnitude greater than G″. Notably, no typical yielding stress point was found within the entire range of stress amplitudes (Fig. 3a, Fig. S3b and S3c, ESI†). However, when the stress was reached to the limit of a applied stress of 3000 or 5000 Pa, the sample was spilled and collapsed rather than be liquefied to a solution that lead to a sudden plummeting of the moduli. This type of response reveals the robust and brittle feature of this supramolecular gel. The gel also showed special bottom-up load-bearing property, one to three spatulas (*ca.* 26 g) were inserted into the gel body and suspended just by holding the test tube (Fig. 3b). The gel body was able to support up to 30-fold its own weight without causing any visible change. To our knowledge, this is the first example that described such unique bottom-up load-bearing strength through the insert of the weights into gel body which probably associate with the solid-like and viscoelastic feature of the gel, although several supramolecular gels with load-bearing abilities in up-down mode have been reported [6, 7c]. A stir bar could also be adhered to the surface of the inverted gel without falling down which confirmed the viscous feature of the gel.
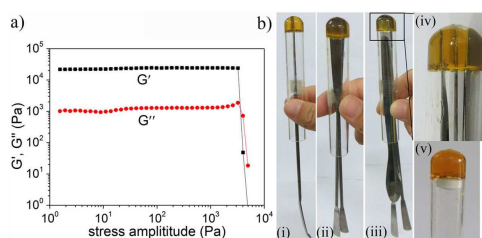

Fig. 3 (a) The stress sweep data of gel **1** (4 %) at a fixed frequency of 1.0 Hz, (b) the bottom-up load-bearing and sticky property of gel **1** (4 %).

Very surprisingly, the fragments of gel **1** could be restored to the gel phase within seconds by adding of DMF or H_2O (Fig. 4). This result gave an indication of the solvent-mediated cooperative hydrogen-bond interactions that stabilized the gel. We rationalized that this particular phenomenon might be related to the swelling behavior of the gel fragments. Subsequently, a swelling experiment was conducted to test this hypothesis. A gel block with original size, 9 mm (length) *8 mm (width), was found to expanded to 12 mm * 10 mm accordingly after immersing into DMF for several minutes (less obvious for height). Also, the same volume solvent could be absorbed by an integral gel upon resting for overnight, which is consistent with the swelling and restoration process (Fig. S4, ESI†). Unexpectedly, the solvent-healed gel displayed extraordinary deformation recovery ability by shaking and re-shaking (Fig. 4a and Movie 1). This process could be repeated at will, without observing any loss of recovery ability. It is reasonable to assume that this observation might be associated with the polymer-like feature of the self-assembled metallogel because the flow of cross-linked polymers always accompany with the deformation. [14] Generally, supramolecular gels formed by noncovalent bonds are extremely sensitive to external stimuli and mostly exhibit reversible sol-gel transition when subjected to shaking or heating. As far as we know, example of such a supramolecular gel with solvent or mechanical stress-induced healing, deformation recovery ability and polymeric feature have not to be reported yet. Further investigation demonstrated that the newly solvent-healed gel almost lost viscoelastic response; however, the viscoelastic moduli were restored to 30% of the original values after aging for several days (Fig. S3d, ESI†). The results here indicated that the healing of this diluted gel quite possibly underwent a minor proportion of recombination of broken bonds and network for maintaining the gel phase firstly to a major proportion after aging. Interestingly, the recovered gel after aging still kept the moldability and self-healing ability (Fig. 5e). The large area of damage of gel **1** at CGC could also be repaired upon adding of H_2O, which also verified the swelling hypothesis. In addition, when the gel was thoroughly cut into a cross rupture (Fig. 4c), it can be healed by adding few drops of H_2O to the damaged surface of the gel, and the healing process could be accelerated by sonication, which is likely resulted from increasing the permeating speed of H_2O. To test the healing result, aqueous solution of methyl red (*ca.* 0.1%) was poured onto the surface of the recovered gel. Although very faint trace of the cross rupture remained, no permeating of the red solution into it was observed, which suggesting the excellent healing property of the self-assembled metallogel and biological similarity to wound healing (Fig. S5, ESI†).

Fig. 4 (a) The solvent-healed and deformation recovery process of the broken gel **1** (4 %, 1 mL DMF), (b) the large area damage of gel **1** (3 %, 0.5 mL DMF) was repaired by adding H_2O (0.25 mL), c) the sonication-assisted healable process of a cross rupture.

Moreover, a 3-cm long self-supporting bridge was constructed by simply joining together the blocks of gel **1** and keeping them in contact for several minutes at room temperature without any external stimuli (Fig. 5b). Interestingly, the gel displayed excellent light transmittance viewed from the yellow shadow of the blocks (Fig. 5a), and even clear words could be seen through the gel (Fig. S6a, ESI†). The resultant bridge is strong enough to hold when suspended horizontally or vertically from a wire (Fig. 5c). Not only the regeneration of reversible non-covalent interactions, but also the reconnection of the network across the interface quite possibly facilitated the autonomic repair property. The gel block also showed a preference for adhering to a razor (Fig. S6b, ESI†), and this sticky feature might assisted the self-healing process. The similar healing behavior was also observed for both of the moulded blocks and the solvent-healed gel blocks (Fig. 5d and 5e). Thus, the self-healing properties of this metallogel can be accomplished by different approaches. Notably, gels **2-4** were also displayed such self-healing capability.
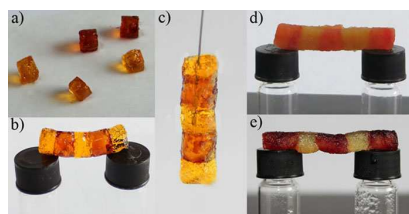
Fig. 5 (a, b) a bridge constructed by connecting freshly prepared blocks of gel **1** can be suspended horizontally and (c) held vertically, (d) a bridge constructed by connecting moulded gel blocks and (e) solvent-healed (DMF) gel blocks. Red objects correspond to metallogel blocks obtained upon doping with aqueous solution of methyl red (*ca.* 0.1%).

In conclusion, we have described the self-healing and moldable materials from a readily prepared supramolecular metallogel system. The material exhibited remarkable deformation recovery and bottom-up load-bearing capability. Furthermore, the macroscopic self-healing process could be achieved by multi accessible approaches when damaged. So far no other self-assembled supramolecular gels have been reported to possess all these features. These results could give key clues to the design of self-healing materials based on non-covalent bond. In addition, we foresee that this kind of metallogels could impart outstanding chemical and physical properties of transition-metal ions, and efforts are now in progress to investigate their catalytic applications.

Notes and references

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1   S. Burattini, B. W. Greenland, D. Chappell, H. M. Colquhoun, W. Hayes, *Chem. Soc. Rev.* **2010**, *39*, 1973.
2   (a) B. J. Blaiszik, S. L. B. Kramar, S. C. Olugebefola, J. S. Moore, N. R. Sottos, S. R. White, *Annu. Rev. Mater. Res.* **2010**, *40*, 179. (b) K. Imato, M. Nishihara, T. Kanehara, Y. Amamoto, A. Takahara, H. Otsuka, *Angew. Chem. Int. Ed.* **2012**, *51*, 1138.
3   (a) P. Cordier, F. Tournilhac, C. Soulie-Ziakovic, L. Leibler, *Nature.* **2008**, *451*, 977; (b) M. Burnworth, L. Tang, J. R. Kumpfer, A. J. Duncan, F. L. Beyer, G. L. Fiore, S. J. Rowan, C. Weder, *Nature.* **2011**, *472*, 334; (c) M. Nakahata, Y. Takashima, H. Yamaguchi, A. Harada, *Nat. Commun.* **2011**, *2*, 511; (d) N. Holten-Andersen, M. J. Harrington, H. Birkedal, B. P. Lee, P. B. Messersmith, K. Y. C. Lee, J. H. Waite, *Proc. Natl. Acad. Sci.* **2011**, *108*, 2651; (e) J. E. Martin, A. J. Patil, M. F. Butler, S. Mann, *Adv. Funct. Mater.* **2011**, *21*, 674; (f) M. Zhang, D. Xu, X. Yan, J. Chen, S. Dong, B. Zheng, F. Huang, *Angew. Chem. Int. Ed.* **2012**, *51*, 7011; (g) E. A. Appel, X. J. Loh, S. T. Jones, F. Biedermann, C. A. Dreiss, O. A. Scherman, *J. Am. Chem. Soc.* **2012**, *134*, 11767; (h) T. Kakuta, Y. Takashima, M. Nakahata, M. Otsubo, H. Yamaguchi, A. Harada, *Adv. Mater.* **2013**, *25*, 2849; (i) L. Huang, N. Yi, Y. Wu, Y. Zhang, Q. Zhang, Y. Huang, Y. Ma, Y. Chen, *Adv. Mater.* **2013**, *25*, 2224; (j) J. R. McKee, E. A. Appel, J. Seitsonen, E. Kontturi, O. A. Scherman, O. Ikkala, *Adv. Funct. Mater.* **2014**, *24*, 2706; (k) M. Guo, L. M. Pitet, H. M. Wyss, M. Vos, P. Y. W. Dankers, E. W. Meijer, *J. Am. Chem. Soc.* **2014**, *136*, 6969; (l) C. Yu, C.-F. Wang, S. Chen, *Adv. Funct. Mater.* **2014**, *24*, 1235; (m) R. J. Wojtecki, M. A. Meador, S. J. Rowan, *Nat. Mater.* **2011**, *10*, 14.
4   (a) S. Dong, Y. Luo, X. Yan, B. Zheng, X. Ding, Y. Yu, Z. Ma, Q. Zhao, F. Huang, *Angew. Chem. Int. Ed.* **2011**, *50*, 1905; (b) X. Yan, D. Xu, X. Chi, J. Chen, S. Dong, X. Ding, Y. Yu, F. Huang, *Adv. Mater.* **2012**, *24*, 362; (c) S. Dong, B. Zheng, D. Xu, X. Yan, M. Zhang, F. Huang, *Adv. Mater.* **2012**, *24*, 3191; (d) X. Yan, D. Xu, J. Chen,; M. Zhang, B. Hu, Y. Yu, F. Huang, *Polym. Chem.* **2013**, *4*, 3312; S. (e) Dong, J. Yuan, F. Huang, *Chem. Sci.* **2014**, *5*, 247; (f) Z. Qi, C. A. Schalley, *Acc. Chem. Res.* **2014**, *47*, 2222.
5   A. Vidyasagar, K. Handore, K. M. Sureshan, *Angew. Chem. Int. Ed.* **2011**, *50*, 8021.
6   P. Sahoo, R. Sankolli, H.-Y. Lee, S. R. Raghavan, P. Dastidar, *Chem. Eur. J.* **2012**, *18*, 8057.
7   (a) S. Roy, A. Baral, A. Banerjee, *Chem. Eur. J.* **2013**, *19*, 14950; (b) S. Basak, J. Nanda, A. Banerjee, *Chem. Commun.* **2014**, *50*, 2356; (c) S. Saha, J. Bachl, T. Kundu, D. D. Díaz, R. Banerjee, *Chem. Commun.* **2014**, *50*, 3004.
8   Q. Wang, J. L. Mynar, M. Yoshida, E. Lee, M. Lee, K. Okuro, K. Kinbara, T. Aida, *Nature.* **2010**, *463*, 339.
9   (a) D. C. Tuncaboylu, M. Sari, W. Oppermann, O. Okay, *Macromolecules.* **2011**, *44*, 4997; (b) X. Chi, D. Xu, X. Yan, J. Chen, M. Zhang, B. Hu, Y. Yu, F. Huang, *Polym. Chem.* **2013**, *4*, 2767.
10   CGCs and other concentrations are expressed in % as 100 × the ratio of the weight of ligand and $Pd(OAc)_2$ (g) to DMF volume (mL).
11   A. Ajayaghosh, R. Varghese, S. Mahesh, V. K. Praveen, *Angew. Chem. Int. Ed.* **2006**, *45*, 7729.
12   T. D. Hamilton, D.-K. Bucar, J. Baltrusaitis, D. R. Flanagan, Y. Li, S. Ghorai, A. V. Tivanski and L. R. MacGillivray, *J. Am. Chem. Soc.* **2011**, *133*, 3365, and references therein.
13   S. Banerjee, N. N. Adarsh, P. Dastidar, *Soft Matter,* **2012**, *8*, 7623.
14   M. T. Shaw, *Introduction to Polymer Rheology*. John Wiley & Sons, Hoboken, New Jersey, **2012**.