Supporting Information

Self-recoverable Dual-network Silicon Elastomer Applied in Cell Adhesives

Hang Lu[a,b], Ziqi Hu[c], Dengxu Wang[d],Kaixuan Chen[b], Shengyu Feng [, a]*

a. Key Laboratory of Special Functional Aggregated Materials & Key Laboratory of Colloid and Interface Chemistry, Ministry of Education; School of Chemistry and Chemical Engineering, Shandong University, Jinan, 250100, P. R. China

b. Zhejiang Wynca Chemical Industry Group Co., Ltd, Hangzhou, 311100,   P. R. China

c. Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials Chemistry and Applica-tions, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

d. National Engineering Technology Research Center for Colloidal Materials, Shandong University, Jinan, 250100, P. R. China
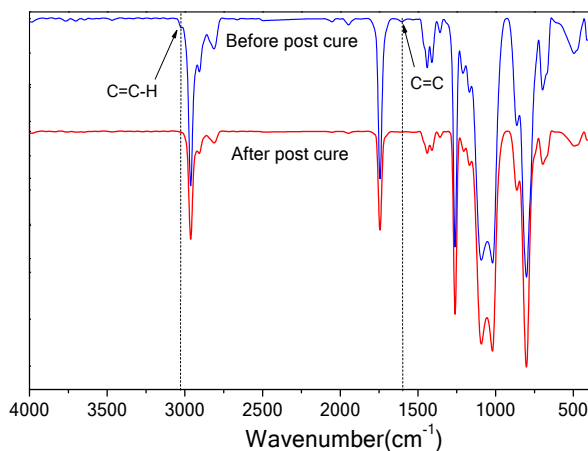
Figure S1 IR Spectrum of the Elastomer Before and After the Post-cure

The aza-Michael addition can proceed in a smooth and catalyst-free way with high yield. However, the concentration and the activity of the reactant in the elastomer were low, which made the crosslinking incomplete. To make the aza-Michael addition complete, post cure was performed.[1] Figure S1 was the IR spectrum of the elastomer before and after the post-cure. Before post cure, C-H stretching vibration band of olefin (3020 cm⁻

^{1}), and C=C stretching vibration band (1603 cm^{-1}) were observed. After post cure at 100

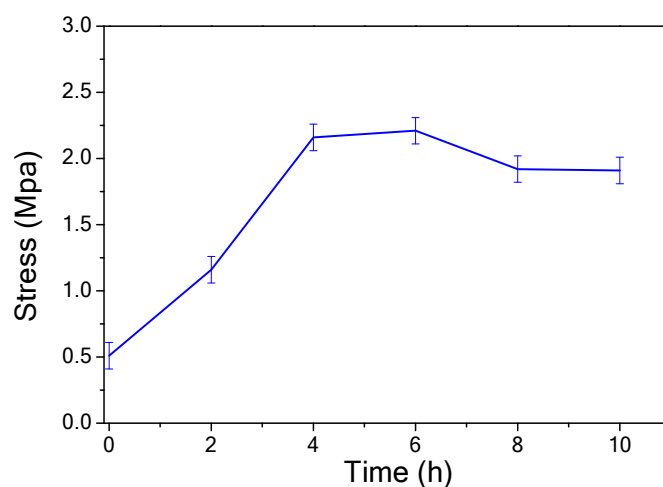℃ for 4 h, the characteristic peaks of olefin were vanished.

Figure S2 The effect of post cure time on stress of the elastomers

Figure **S2** showed the effect of post-cure time on stress of the elastomers at 100 ℃. The results indicated that the post cure can improve the stress of the elastomer, and when the post cure time was 4-6 hours, the tensile strength can reach the max value. The tensile strength was lowered when the post cure time was more than 6 hours, which caused by thermal ageing.

Table S1 The Tensile Stress of the Elastomers with Dual-network or Different Metal Ion

Sample	Metal ion	Tensile Strength (MPa)
E-14-880	-	≈ 0
E-14-Fe-4-0	Fe^{3+}	< 0.5
E-14-Fe-4-880	Fe^{3+}	2.16
E-14-Zn-4-880	Zn^{2+}	0.65
E-14-Cu-4-880	Cu^{2+}	< 0.5
E-14-Ni-4-880	Ni^{2+}	< 0.5
E-14-Ca-4-880	Ca^{2+}	< 0.5

Sample	Metal ion	Tensile Strength (MPa)
E-14-Co-4-880	Co^{2+}	< 0.5
E-14-Cr-4-880	Cr^{2+}	< 0.5

Table S1 was the tensile stress of the elastomers with dual-network or different metal ion. The results suggested that the dual-network enhanced the tensile stress effectively. Fe^{3+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Ca^{2+}, and Co^{2+} were used as physical crosslink agents.[2-5] During the investigation, the elastomers crosslinked by Fe^{3+} showed a good mechanical property. The charge/radius of Fe^{3+} was the largest. Therefore, Fe^{3+} can form stable coordination bonds. In this work, Fe^{3+} was chose as the physical crosslink agent.

Table S2 Tensile Strength of the Elastomers with Different Amount of Fe^{3+}

Sample	Base Gum	$\dfrac{n(N+C=O)}{n(Fe^{3+})}$	Tensile Strength （MPa）
E-21-Fe-10-880	E-21	10	0.64
E-21-Fe-8.33-880	E-21	8.33	0.76
E-21-Fe-7.5-880	E-21	7.5	0.75
E-21-Fe-6.67-880	E-21	6.67	0.84
E-21-Fe-5-880	E-21	5	1.03
E-14-Fe-9.67-880	E-14	9.67	0.65
E-14-Fe-8.1-880	E-14	8.1	0.77
E-14-Fe-7.25-880	E-14	7.25	0.84
E-14-Fe-6.45-880	E-14	6.45	1.28
E-14-Fe-5.64-880	E-14	5.64	1.47
E-14-Fe-4.5-880	E-14	4.5	1.85
E-14-Fe-3-880	E-14	3	1.87
E-11-Fe-5.25-880	E-11	5.25	1.97
E-11-Fe-5-880	E-11	5	2.34
E-11-Fe-4.5-880	E-11	4.5	2.09
E-11-Fe-4-880	E-11	4	2.47

Sample	Base Gum	$\dfrac{n\,(N\,+\,C=O)}{n\,(Fe^{3+})}$	Tensile Strength （MPa）
E-11-Fe-3.5-880	E-11	3.5	2.97
E-11-Fe-3-880	E-11	3	3.45

The wt% of Fe^{3+} in E-14-Fe-4.5-880 and E-11-Fe-5.25-880，or in E-21-Fe-5-880 and E-14-Fe-7.25-880 were equal.
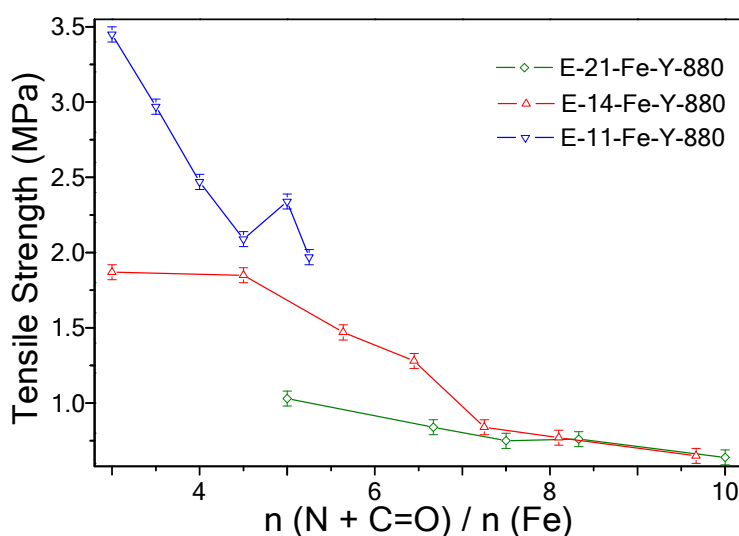

Figure S3 The Effect of Fe^{3+} on Tensile Strength of the Elastomers

Because of the poor compatibility of Fe^{3+} and polysiloxane, uniform elastomers were obtained when the value of n (N + C=O)/n (Fe^{3+}) was over 3. According to the orbital hybridization, Fe^{3+} can form d^2sp^3 hybrid orbitals, which can form 6 coordination bonds. However, the tensile strength of the elastomers was enhanced as the Fe^{3+} content was increased, even the value of n (N + C=O)/n (Fe^{3+}) was between 3 and 6. The steric hindrance and entanglement of the polymer chain reduced the efficiency of coordination. Meanwhile, slightly excess $FeCl_3\cdot6H_2O$ can act as a filler which can increase the tensile strength of the elastomers.

The efficiency of the modification was about 75 %, and the Mn of P-11, P-14, and P-21were 69800, 72500, and 78600, respectively. Thus, the effects of base gum on the elastomers were mainly caused by the amount of the N and carbonyl groups in base gum. As showed in Table S2 and Figure S3, the tensile strength of the elastomer with the same value of n (N + C=O)/n (Fe3+) was changed as followed: E-11-Fe-Y-880 > E-14-Fe-Y-880 > E-21-Fe-Y-880. The more ligands in the base gum, the more coordination bonds formed in the elastomers, which increased the tensile strength. When the wt% of $FeCl_3 \cdot 6H_2O$ remained unchanged (E-14-Fe-4.5-880 and E-11-Fe-5.25-880, E-21-Fe-5-880 and E-14-Fe-7.25-880, the amount of coordination bonds formed by Fe^{3+} was the same theoretically), the tensile strength of the elastomers were almost the same. However, the Mn of the base gum and the random error caused the difference of the tensile strength.

Table S3. The ratio of effective network chain density calculated from DMA

Temperature (℃)	-20			0			20			50		
Sample	1	2	3	1	2	3	1	2	3	1	2	3
$\frac{n(N + C = O)}{n(Fe)}$	3.5	4	4.5	3.5	4	4.5	3.5	4	4.5	3.5	4	4.5
E'	30.15	21.10	15.57	13.46	9.23	7.38	8.25	5.70	4.45	5.29	3.70	2.84
N1 : N2 : N3	1.94: 1.36 : 1			1.82 : 1.25 : 1			1.85 : 1.28 : 1			1.86 : 1.30 : 1		

Sample 1, 2, 3 represent E-11-Fe-3.5-880, E-11-Fe-4-880, and E-11-Fe-4.5-880, respectively.

The effective network chain density was calculated by using equation as follows:

$$E' = \lambda NRT$$

Where λ is the elastomer based constant, and R and T represent the gas constant and absolute temperature, respectively.

The ratio of effective network chain density can be obtained as follows:

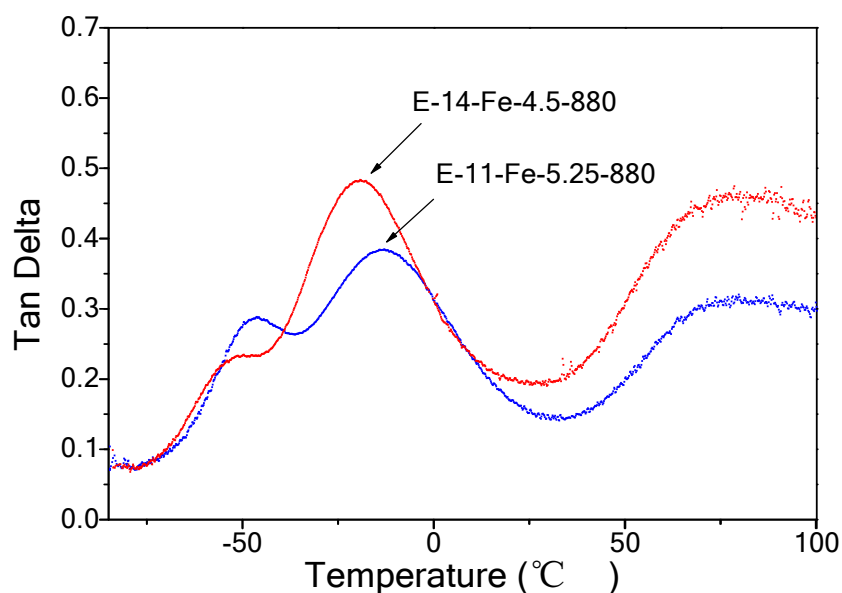$$N = \frac{E'}{\lambda RT} \rightarrow N_1 : N_2 : N_3 = E'_1 : E'_2 : E'_3$$

Figure S4 The Dynamic Tan δ – Temperature Cruve of E-11-Fe-5.25-880 and E-14-Fe-4.5-880

Figure S4 showed the difference between E-11-Fe-5.25-880 and E-14-Fe-4.5-880 (the wt% of $FeCl_3 \cdot 6H_2O$ in E-11-Fe-5.25-880 and E-14-Fe-4.5-880 were the same). $-Si(Me)_2O-$ was a flexible unit which can lower the T_g of the polymer. The content of $-Si(Me)_2O-$ unit in E-14 was higher than E-11. Thus, the T_g of E-14-Fe-4.5-880 was lower than the E-11-Fe-5.25-880. However, the peak positions of the curves at high temperature attributed to the dissociation of the coordination were the same, which meant the properties (the amount of coordination bonds formed by Fe^{3+}) of the coordination in the elastomers were the same.
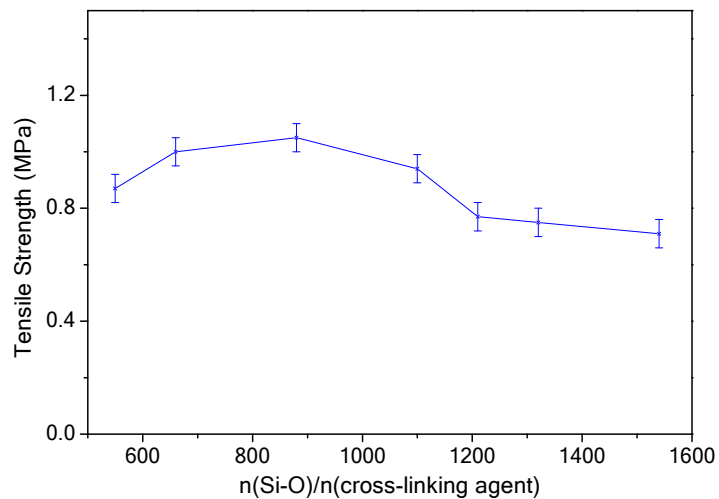
Figure S5 The Effect of Cross-linking Agent on Tensile Strength of the Elastomers

The Figure S5 indicated that when the value of Z was 880, the elastomers possessed good mechanical properties.

The spin Hamiltonian of the system can be described as:

$$\hat{H} = D\left[\hat{S}_z^2 - \frac{S(S+1)}{3}\right] + E\left(\hat{S}_x^2 - \hat{S}_y^2\right) + g_{iso}\mu_B \boldsymbol{B}\hat{\boldsymbol{S}}$$

where the first two terms describe the rhombic symmetry ZFS and the last term is the Zeeman effect.
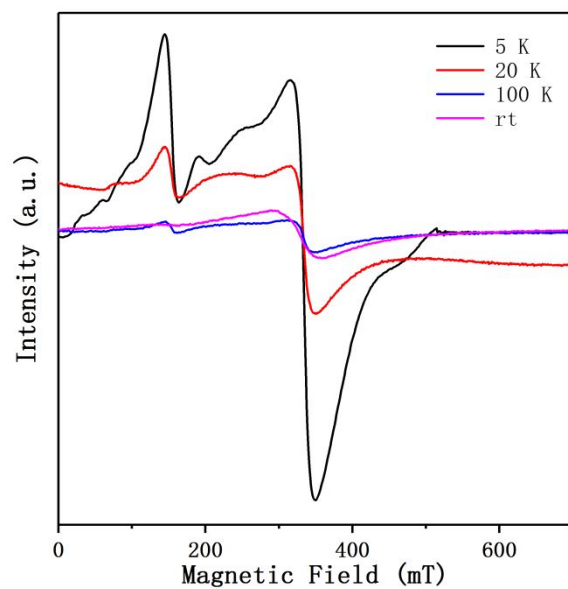
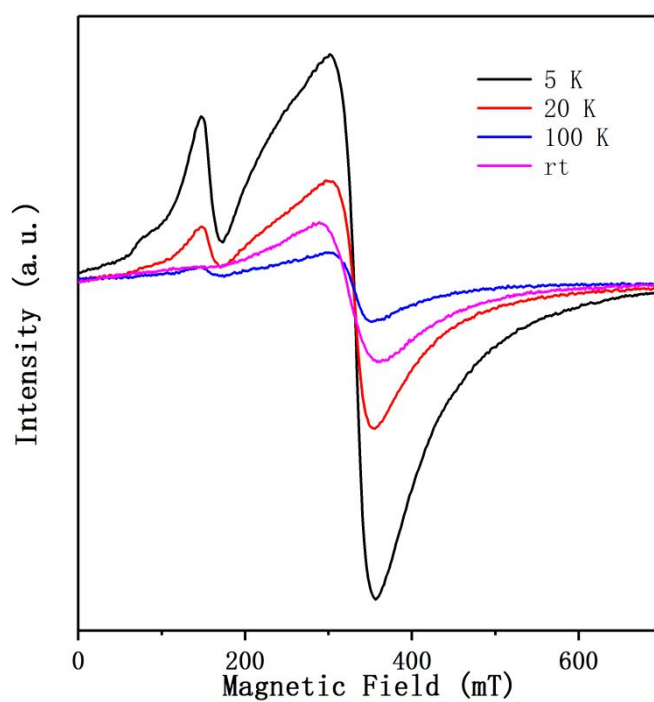**Figure S6** The the ZFS absorptions of E-11-Fe-4.5-880.
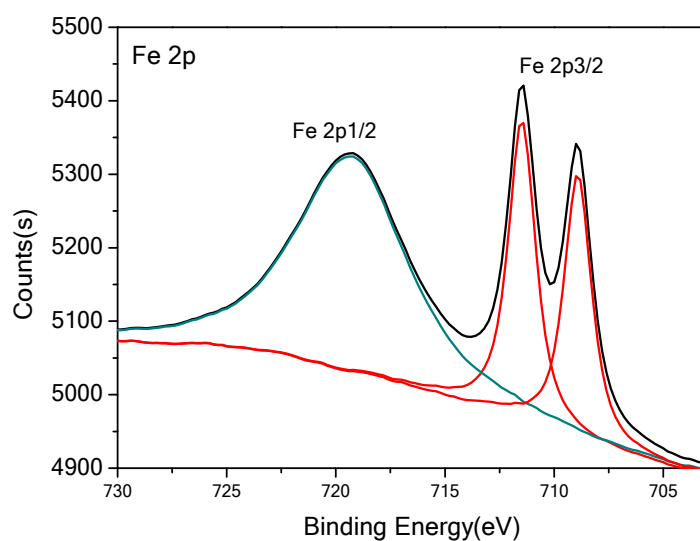

Figure S7 The the ZFS absorptions of E-11-Fe-3-880.

Figure S8. XPS of the Fe 2p spectral region

The peaks of Fe 2p were located at 708.9, 711.5 and 719.3 eV. The peak at 719.3 eV belonged to the Fe 2p1/2. The peak at 711.5 eV attributed to coordinated Fe(III), and the peak at 708.9 eV attributed to $FeCl_3$.
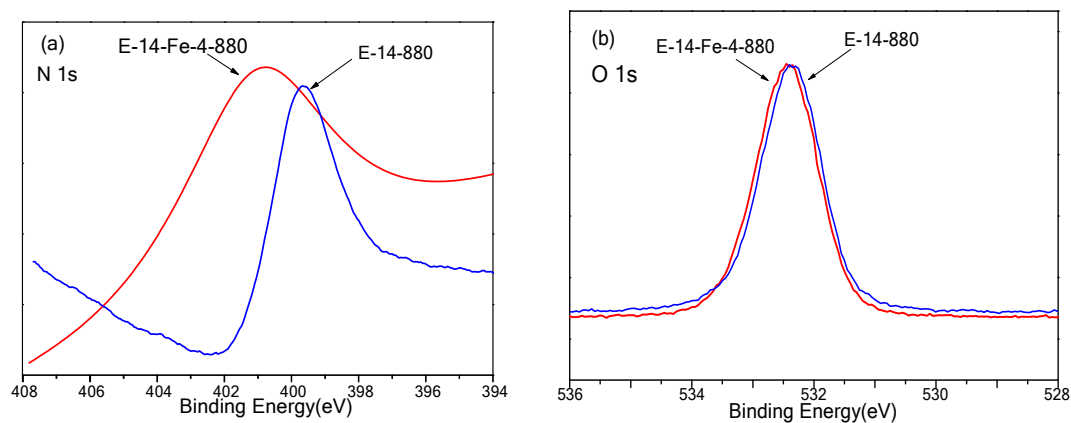

Figure S9. XPS of the N 1s(a) and O 1s(b) spectral region

The coordination made the binding energy of N 1s and O 1s shift to high region.
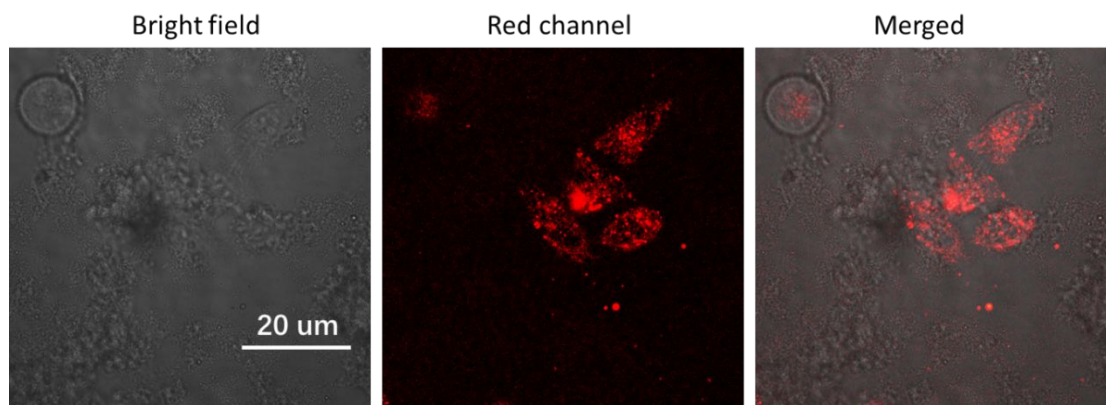
| Bright field | Red channel | Merged |

Figure S10. HeLa cells culturing on the upper surface of controlled sample C2. The images of cells spread on the surface of the elastomer, magnification: 40×, scale: 20 μm.

Note:

Two controlled elastomer samples were fabricated as control experiments. The formulas were similar to E-11-Fe-4.5-880. However, C1 was constructed without Fe^{3+}, C2 was constructed with TS-530 as filler of 10 % mass ratio. Cell experiments were conducted on C1 and C2, respectively. Related discussion was added to the Supporting information. We found that C1 was not so stable when soaked in cell culture medium, and swelling occurred. Therefore, elastomers without Fe^{3+} were not suitable for cell imaging. However, C2 was stable when soaked in cell culture medium. MitoRed was then selected as the dye for cells. As shown in Figure S10, the cultured HeLa cells grew well on the upper surface of C2. The results indicated that the polysiloxane-based elastomers with filler could be applied in bioimaging. The results indicated that the usage of Fe^{3+} as cross-linking point render the elastomer better biocompatibility, while, the filler showed negligible effect to the biocompatibility of the sample.

AUTHOR INFORMATION

Corresponding Author

Shengyu Feng*

E-mail: fsy@sdu.edu.cn

Reference

1. Feng, L.; Zhou, L.; Feng, S., Preparation and characterization of silicone rubber cured via catalyst-free aza-Michael reaction. RSC Adv. **2016,** *6*, 111648-111656.

2. Cao, J.; Zhang, X.; Lu, C.; Luo, Y.; Zhang, X., Self‑Healing Sensors Based on Dual Noncovalent Network Elastomer for Human Motion Monitoring. Macromol. Rapid Commun. **2017,** 38, 1700406-1700412.

3. Zou, X.; Xing, K.; Zhang, R.; Zhang, Y.; Wang, X.; Wu, Q.; Chen, T.; Sun, P., Viscoelasticity and Structures in Chemically and Physically Dual-Cross-Linked Hydrogels: Insights from Rheology and Proton Multiple-Quantum NMR Spectroscopy. *Macromolecules* **2017**, *50*, 9340-9352.

4. Jia, X. Y.; Mei, J. F.; Lai, J. C.; Li, C. H.; You, X. Z., A Highly Stretchable Polymer that Can Be Thermally Healed at Mild Temperature. Macromol. Rapid Commun. **2016,** *37*, 952-956.

5. Lin, P.; Ma, S.; Wang, X.; Zhou, F., Molecularly engineered dual-crosslinked hydrogel with ultrahigh mechanical strength, toughness, and good self-recovery. Adv. Mater. **2015,** *27*, 2054-2059.