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Rong Fu,^a Junying Zhang,^a Shaojie Liu,^a Xing-Dong Xu*^a and Shengyu Feng ^a

Facile construction of double network cross-linked luminescent supramolecular elastomer from hydrosilylation and pillar[5]arene

Reticulated copolymer hosts pillar[5]arene crosslinked with poly(dimethylsiloxane) (PDMS) were synthesized for the facile construction of double network crosslinked elastomer upon noncovalently cross-linking with tetraphenyethylene (TPE)-based tetratopic guests through host-guest interactions. The obtained sample strips represented better mechanical property and luminescent capability.

host-guest recognition

Polymeric materials have increasingly found extensive applications, under high quality standard conditions for such as aerospace and organisms which put high demands on the thermal stability and biocompatibility of the materials.¹ Polydimethylsiloxane (PDMS) is a typical rubbery material that consists of soft and flexible polymer chains with cross-linking points and possesses the merits of tunable mechanical strength, high chemical stability, great biocompatibility and inherent flexibility at broad temperature ranges.² Through reasonable crosslinking design, it has been attracted great attention in the applications of electronic skins, artificial muscles, and sensors, especially for stretchable devices, etc.³ However, the mechanical properties still needs to be further enhanced when compared to some load-bearing tissues.⁴ Inspired by the fact that biological processes frequently involve a supramolecular self-assembly event followed by the formation of a covalent bond between two building blocks, recent research efforts have focused on the development of a new strategy by combining supramolecular self-assembly with covalent chemistry for the construction of artificial architectures that maybe able to solve the above mentioned problem.⁵ For example, Suo and co-workers⁶ reported the extremely stretchable and tough hydrogels by mixing two types of crosslinked polymer forming ionically and covalently crosslinked networks. To the best of our knowledge, this

^{a.} National Engineering Research Center for Colloidal Materials, Key Laboratory of Special Functional Aggregated Materials of Ministry of Education, Shandong University, Jinan 250100, Shandong, China. E-mail: xuxd@sdu.edu.cn.

strategy has rarely been used to enhance the mechanical properties of elastomers, especially silicone elastomers.⁷

A seminal approach to fabricate double-network elastomers is introduction of non-covalent bonds such as the supramolecular macrocycle-based host-guest chemistry, which could induce significantly enhancement of toughness of materials due to the host-guest interactions between macrocycles and guest molecules.⁸ Pillar[n]arene, as an important class of macrocyclic hosts first reported by Ogoshi and coworkers in 2008, are attracting more and more attention.⁹ Among the pillar[n]arene family, pillar[5]arene take up a lot of advantages: 1) bind neutral molecules in organic solvents due to the electron-rich cavity; 2) could provide even 10 functionalized reaction sites; and 3) rigid structure donated stiff component in the fabrication of functional materials, and have showed potential in sensors, catalysts, supramolecular gels, separation and storage. ¹⁰

Furthermore, a luminous macrocycle guest would bring silicon elastomers with luminescent capability. Tetraphenylethylene (TPE) is a well-known AlEgen due to its quite prominent aggregation-induced emission (AIE) properties and facile preparation.¹¹ Some TPE-based materials with efficient AIE luminescence characteristics have been reported with broad applications in stimuli-responsive systems. Therefore, they are very advantageous for the fabrication of various AIE systems and devices for a wide range of applications in different aggregate forms.¹² Herein, based on our previous studies in luminescent materials¹³ and organosilicon materials¹⁴, we designed and synthesised a pillar[5]arene-PDMS copolymer, denoted as P5-PDMS from hydrosilylation reaction as the first cross-linking network. TPE-based tetratopic guests with cyanogroup, that is TPECN, are employed as binders to assemble with the as-prepared polymers via host-guest interactions, fabricating a soft component of noncovalent bonds. This supramolecular polymer networks system works by covalent and non-covalent bonds together to form a double-network cross-linked elastomer and committed to make a luminescent film for potential applications.

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To elucidate the AIE properties of the newly designed molecule TPECN, fluorescence spectra were measured as

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shown in Fig. 1. In the fluorescence measurement, **TPECN** exhibited an archetypal AIE property. In a good solvent THF, it exhibits a clear solution state without fluorescence emission.

The reason is that the rotations of the peripheral phenyl rings against the olefinic stator around the single-bond axes consume the excited-state energy. And the aggregation caused by the addition of H₂O (Fig. 1a) and PDMS (Fig. 1b) clearly increased the fluorescence intensity to its maximum at 506 nm. When the volume of H_2O or PDMS in the mixture reaches 95%by degrees, the excited state energy consumption by nonradiative pathways is blocked as a result of the effect of the restricted intramolecular rotation (RIR), vitalizing strong emission to the maximum.11, 15 With the addition of poor solvent, it can be clearly observed from Fig. 1c that the fluorescence intensity at 506 nm showed a trend of linear change. Among them, the peak of Fig. 1b between 400-450 nm is due to the weak luminescent of PDMS which is an interference that can be eliminated. Therefore, TPECN is a typical AIE molecules whose irradiative mechanism is based on the theory of restriction of intramolecular rotations (RIR), which could be well regulated through the combine of supramolecular macrocycles and AIEgens.



Scheme 1 Schematic illustration of the construction of fluorescent supramolecular silicon polymers.

Pillar[5]arene, as a typical supramolecular macrocycles, is capable of binding toward neutral guest molecules in organic solvents, such as cyano derivatives (**TPECN**) which were selected as neutral guest molecules due to their high binding affinity toward pillar[5]arenes in certain organic solvents.¹⁶ In this system, the host-guest properties of **P5-PDMS** and **TPECN** were studied in CDCl₃ by ¹H NMR spectroscopy using **P5** and a **TPECN** as model host and guest compounds. As is shown in Fig.

2, the complexation is a slow-exchanging system on the proton NMR time scale. The resonance of protons in 3 benzene24H2, methylene and Vinyl H2, H3, H4, H5, H6 from P5, the aromatic unit Ha and Hb of **TPECN** were clear broadened and displayed a slightly downfield shift, due to the deshielding effect on protons exposed outside the electron-rich cavity of P5. While the proton signals of Hc, Hd, He, Hf and Hg of **TPECN** were broadened, and partly shifted upfield remarkably, due to the shielding effect on protons drilling into the electron-rich cavities of P5. It is worth noting that there is part of the proton signals of Hc, Hd, He, Hf and Hg almost unchanged, suggesting that both complexation and uncomplexation between **TPECN** and **P5** exist at the same time.



Fig.1 Fluorescence spectra of **TPECN** (10 μ M, λ ex = 380 nm) in mixed solvent of THF/H₂O(a), and THF/PDMS(b), and a plot of fluorescence intensity of TPECN (10 μ M) at 506 nm in THF/H₂O(PDMS) mixtures with different H₂O(PDMS) fractions. (d) Fluorescent picture

With the newly designed building blocks in hand, the double network cross-linked supramolecular elastomer from covalent and non-covalent bonds was investigated. In order to construct the covalent bond network which bears a hard segment that acts as a skeleton, P5 and H-terminated PDMS were reacted through efficient hydrosilylation reaction, which was widely used in industry. The adequacy of cross-linking could be demonstrated by FT-IR spectra of P5-PDMS and P5-TPECN-PDMS elastomers which are shown in Fig. S1 in ESI. In FT-IR spectra, peaks at 1649cm⁻¹, 3016.8 cm⁻¹ and 3077.88 cm⁻¹ ¹ are not observed, which indicated that the ethylene bonds on P5 on the P5-PDMS elastomer has disappeared, proved that P5 and PDMS are almost completely crosslinked by covalent bonds. On the other hand, we envision that the AIEgens guests we introduced to covalent polymers systems can not only help achieve high emission efficiency, but also improved the flexibility of the elastomer by weak non-covalent bonds.

The thermal stability of the elastomer is of vital importance in the application since their decomposition leads to a decrease in device performance. Therefore their thermal stabilities were

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measured by thermogravimetric analysis (TGA) at a heating rate of 100°C/min under N₂. The thermogravimetric weight loss curves for all compounds show that the decomposition of the complexes progresses similarly from Fig. 3(a). The TGA curves indicate that **PDMS**, **P5-PDMS** and **P5-TPECN-PDMS** decompose above 346°C, 404°C and 402°C, respectively, which means that the thermal property was scarcely influenced with the addition of guest molecules. The weight loss step may be due to the decomposition of the organic groups and the breaking of the polysiloxane main chain.



8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0 **Fig. 2** ¹H NMR spectra (CDCl₃, 400 MHz, 298 K) of (a) 20 mM **P5**; (b) 5 mM **TPECN** and 20 mM **P5**; (c) 5 mM **TPECN**.



Fig. 3 (a) TGA of PDMS, P5-TPECN-PDMS and P5-TPECN-PDMS. (b) Tensile tests measured at room temperature for elastomers P5-PDMS and P5-TPECN-PDMS, test speed=20mm/min. (c) Typical successive loading-unloading tensile tests for ten runs at room temperature for elastomers P5-TPECN-PDMS, test speed=20mm/min. (d) Typical Loadingunloading compressive tests measured at room temperature for elastomers P5-PDMS and P5-TPECN-PDMS, test speed=5mm/min.

The mechanical property of the elastomeric samples which was conducted by tension experiment at room temperature is

shown in Fig. 3. The mechanical property was enhanced dramatically upon the addition of **TPECN** into the **CPS-PDMS** network (**P5-TPECN-PDMS**). As we can see from the strain-stress curve in Fig. 3b, from the elastomer **P5-PDMS** to **P5-TPECN-PDMS**, the maximum stress increased from 240 KPa to 375 KPa, while the maximum strain increased from 100% to 215%. The enhanced mechanical properties could be explained by the fact that in addition to the covalent bonds of the **P5-PDMS** network, the non-covalent cooperativity of host-guest interaction plays a considerable role.

The internal evolution in loading–unloading cycles is investigated further to search out the elastomers' fatigue resistance and resilience capabilities. Typical tensile (20 mm/min) and compressive (5 mm/min) loading–unloading tests are implemented to achieve this purpose. In the consecutive tensile mode in Fig. 3c, the elastomer **P5-TPECN-PDMS** shows favourable resilience and fatigue resistance where each cycle nearly coincides with others, indicating energy dissipation was rare during deformation. Even increasing the number of cycles to 10 of the force, the samples still show good anti-fatigue behaviour. In the compressive tensile mode in Fig. 3d, elastomers **P5-PDMS** and **P5-TPECN-PDMS** both show small hysteresis loop, furthermore, **P5-TPECN-PDMS** has better compression strength (2.25 MPa) compared to **P5-PDMS** (1.75 MPa).



Fig. 4 SEM micrographs of **P5-PDMS** (a) and **P5-TPECN-PDMS** (b); (c) Contact angles of the elastomers **P5-TPECN-PDMS**. (d) film display.

Homogeneous surface morphologies of the upper surface of the silicone elastomers were presented in both **P5-PDMS** (a) and **P5-TPECN-PDMS** (b) from SEM micrographs which could further confirm the adequacy of cross-linking, as is shown in Fig. 4. Likewise, bonding **TPECN** to the silicone elastomer does not affect the morphology, that is, phase separation did not occur when **TPECN** were incorporated. On this homogeneous surface, static contact-angle analysis was performed to study the effect of crosslinking on the silicone elastomer hydrophilic performance. Silicone elastomer is typically a hydrophobic material with a water contact angle of approximately

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 $109\pm0.1.^{17}$ The contact angles of the **P5-TPECN-PDMS** elastomers were tested by a contact angle analyzer with distilled water (Fig. 4c), suggesting the novel luminescent elastomers obtained have similar contact angles compared with traditional silicone rubber. The as-prepared material can be made into a shape-processable film which shows strong luminescence performance (Fig. 4d the left two). The LED bulb (395-400nm) is purple to the naked eye (Fig. 4d the middle one). And then we apply the sample film to the surface of the small bulb, the small bulb coated with the sample film emits green fluorescence excited by the ultraviolet light of the small LED bulb, which is shown at the far right of the Fig. 4d.

In summary, a newly designed luminescent supramolecular elastomer was successfully fabricated based on a double network crosslink strategy. The fluorescence properties of the elastomer were achieved via host-guest chemistry based on the classical RIR mechanism. And in the elastomer network, the covalent bond of P5-PDMS acts as a hard part to act as a high-strength skeleton, simultaneously, the soft non-covalent bond imparts flexibility to the elastomer, this double network crosslink strategy extremely improved the mechanical properties of silicone elastomers. We believe that the marriage of AIE molecules (TPECN) and P5-PDMS copolymers will not only impart supramolecular polymer materials with stable structure and thermodynamic properties, mechanical behavior, and remarkable fluorescent properties, but may also guide a new way to enhance mechanical properties for silicone elastomers with fascinating structures, functions, and applications.

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Conflicts of interest

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There are no conflicts to declare.

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4 | J. Name., 2012, 00, 1-3

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