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## COMMUNICATION

## A Self-healing PDMS Polymer with Solvatochromic Property

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

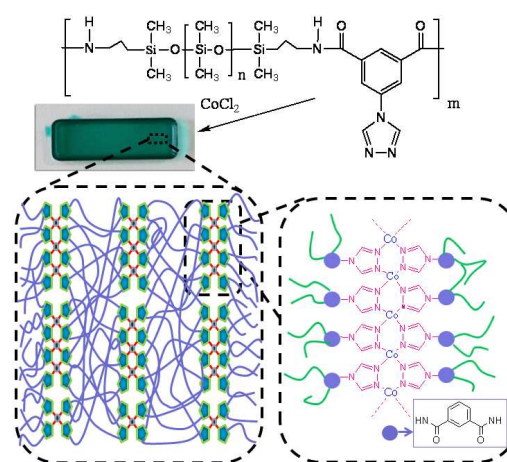
**Coordination bond is effective for constructing functional self-healing materials due to the tuneable bond strength and metal-ion-induced functionalities. In this work, we incorporate a Cobalt(II) triazole complex into polydimethylsiloxane (PDMS) matrix. The resulting polymer show solvatochromic behaviour as well as self-healing properties.**

Most natural biomaterials have an innate ability to self-heal or self-repair upon encountering damages. For example, a minor wound on human skin can be completely healed over time. To mimic the self-healing properties of natural biomaterials and extend the lifetime of the material in numerous applications, many synthetic self-healing polymers which can repair the internal and external damages have been developed.<sup>1</sup> The initial polymeric self-healing materials relied on micro-encapsulated healing agents within the bulk polymer. Due to the consumption of the encapsulated agents, the repair in such system is not repeatable.<sup>2,3</sup> To solve this problem, reversible bonds (such as alkoxyamine,<sup>4</sup> disulfide<sup>5,6</sup>), cross-linking reaction (such as diels-alder reaction,<sup>7,8</sup> radical dimerization reaction,<sup>9</sup> cycloaddition reaction<sup>10,11</sup>) or weak dynamic bonds (such as hydrogen bonds,<sup>12-16</sup>  $\pi$ - $\pi$  stacking interactions,<sup>17-19</sup> host-guest interactions<sup>20,21</sup>) are typically incorporated into polymers as cross-linkages so that they will break first upon damaging and reform after external stimuli, leading to repeatable self-healing.<sup>22-24</sup>

Recently, coordination bond has been demonstrated to be effective for constructing high efficient self-healing.<sup>25-32</sup> The strength of coordination bond is between covalent bond and van der Waals' interactions and most importantly, they can be tuned. By careful selection of the combination of ligand and metal ion, it is possible to tune the bond strength into weak and dynamic which are favourable for self-healing. Moreover, with the introduction of metal ions into polymer matrix, the polymer

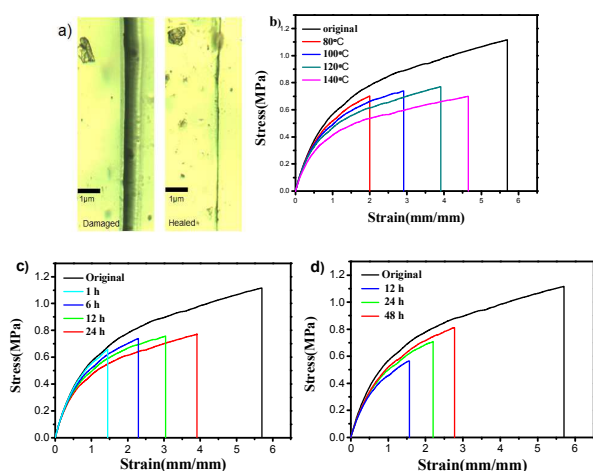
can show various functions such as chromism, luminescence, magnetism, and nonlinear optics.

Cobalt(II) can coordinate with 1,2,4-triazole or triazole derivatives to form two kinds of Cobalt(II) coordination polyhedron: distorted octahedron<sup>33,34</sup> and tetrahedron.<sup>35</sup> The two coordination modes can be reversibly transformed upon external stimuli (such as heating, cooling or adding solvents), thus may provide a possibility for self-healing. In this work, we incorporate a Cobalt(II) triazole coordination complex into polydimethylsiloxane (PDMS) matrix (Scheme 1). Upon damaging, the polymer film can be healed upon heating. Moreover, the colour of the film changed from blue to light pink upon dipping into water or methanol due to the change of coordination number of Co(II) from 4 to 6. More interestingly, owing to the reconfiguration of Co(II)-N<sub>triazole</sub> coordination bond during the solvent-induced chromic process, the damaged film can be healed at room temperature if the cut surface were pre-treated by dipping into methanol solvent.



Scheme 1 Structure and preparation of the chromic and self-healing polymer.

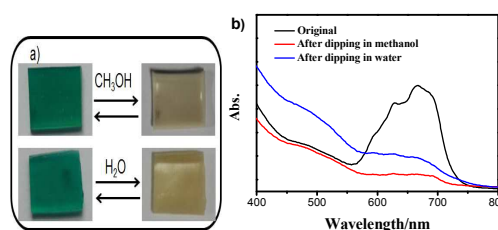
The synthesis of the polymer is described in detail in the experimental section. Briefly, the triazole-containing PDMS (TIA-PDMS) polymers were prepared by crosslinking between bis(3-aminopropyl) terminated poly(dimethylsiloxane) and 5-(4H-1,2,4-triazol-4-yl)isophthaloyl dichloride. Subsequently, the TIA-PDMS polymers were coordinated to Co(II) by a ligand substitution reaction with  $\text{CoCl}_2$  (Figure S1, †ESI). A ligand to metal molar ratio of 2:1 was used based on literature and UV-Vis titration results (Figure S2). TGA and DSC analysis showed that the polymer have a  $T_g$  below  $-100\text{ }^\circ\text{C}$  is thermally stable below  $200\text{ }^\circ\text{C}$ . The mechanical property of the as prepared film (Co-TIA-PDMS) was measured in air, at room temperature, via tensile-strain tests. The as prepared film can be stretched to 560% of its original length and have a Young's modulus of  $1.12\text{ MPa}$ , which is significantly higher than typical self-healing material. The self-healing property of the polymer is illustrated in Figure 1. The healing property was evaluated by both microscopy and tensile test. As shown in Figure 1a, the notch on the film almost disappeared after healing at  $120\text{ }^\circ\text{C}$  for 24 h although distinct healed scars are still visible. In a more quantitative way, the healing efficiencies were evaluated by tensile-stress curves. It can be seen from Figure 1(b,c) and Table S1 (†ESI) that healing efficiencies are a function of healing time and healing temperature. Longer healing time and higher healing temperature will result in higher healing efficiencies. However, the toughness of the film decreased upon continuous heating at high temperature. This is due to that the uncoordinated Co(II) ionic clusters were formed during heating and healing, thus leads to its incomplete insufficient crosslinking.



**Fig. 1** The self-healing property of the Co-TIA-PDMS film. a) Microscopic image of the film before and after healing at  $120\text{ }^\circ\text{C}$ ; b) The stress-strain curves of the film healed at different temperature for 24 h; c) The stress-strain curves of the film healed at  $120\text{ }^\circ\text{C}$  for different time. d) The stress-strain curves of the film healed at RT with pre-treatment by methanol.

The as prepared polymer film also show solvatochromic properties. When dipped into water and methanol, the colour of the film changed from blue to light pink (Figure 2a). UV-Vis diffuse reflectance spectroscopy revealed that the main bands of the complexes had significant changes after treating with water or

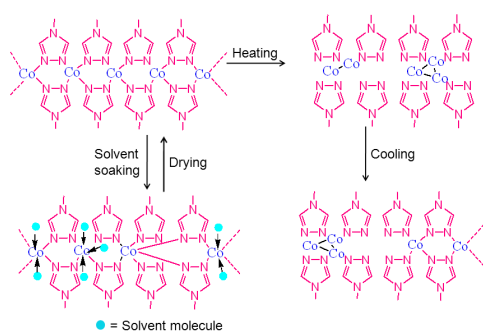
methanol (Figure 2b). The original film displays optical bands at 627, 667 and 689 nm, which is similar with those in solution (Figure S2, †ESI) and characteristic for four-coordinated tetrahedral Cobalt(II) complex.<sup>35</sup> After dipping into water or methanol solvent, the bands at 627, 667 and 689 nm almost disappeared. The resulting spectra are typical for six-coordinated octahedral Cobalt(II) complexes. The light pink film can return to its original colour through heating for several minutes or exposure in air for hours. Several other solvents were also investigated, but only water and methanol show distinct chromic behaviour (Figure S3, †ESI).



**Fig. 2** a) Photograph of solvatochromic process; b) UV-Vis diffuse reflectance spectroscopy for samples before and after dipping into solvents.

As the coordination of Co(II) ion changed between four-coordinated to six-coordinated during the solvatochromic process, we envisaged that such a reversible change of coordination configuration may facilitate the self-healing. Therefore we investigated the effect of solvent pre-treatment on self-healing properties. We dipped the cut film into methanol till its colour change from blue to light pink, and then exposure the film in air at room temperature for different times. The damaged film can be healed at room temperature (Figure S4, †ESI). The colour of the healed film turned back to blue again. The colour change can be used to monitor the self-healing process through naked-eye. The toughness of the healed film was not reduced since no healing is needed, as shown in Figure 1(d). Moreover, in comparison to the film after high temperature healing, which show indistinct chromic behaviour upon dipping into water or methanol, the film after methanol-assisted room temperature healing show the same chromic properties as the original ones.

Scheme 2 illustrates the difference of self-healing mechanism with and without methanol pre-treatment. For self-healing without methanol pre-treatment, the healing is due to formation of ionic clusters.<sup>29</sup> The crosslinking units consist of a doubly positively charged Co(II) centers, which could trigger the formation of ionic clusters. Owing to the insufficient mobility of ionic clusters in the polymer matrix, some Co(II) ions are unavailable for bond reformation upon heating and healing. Therefore, heating healed films show lower toughness due to insufficient crosslinking. However, for self-healing with methanol pre-treatment, the healing is due to the reversible transformation of coordination pattern of Cobalt(II) between four-coordinated to six-coordinated. During this process, some of the Co(II)- $\text{N}_{\text{triazole}}$  bonds are disassociated and exchanged, thus leading to the healing of the damaged films. As the Co(II) complexes are not fully disassociated during this process, no free Co(II) ions or ionic clusters are generated and therefore the toughness of the healed are not significantly reduced.



Scheme 2. The possible self-healing mechanism after dipping into methanol

In summary, we have developed a self-healing polymer with solvent-induced chromic property film by incorporation of a Cobalt(II) triazole complexes into PDMS matrix. The preparation of the polymer is very simple and controllable. The self-healing property is dependent on healing time and temperature. The polymer film can change colour from blue to light pink upon dipping into water or methanol solvents due to the coordination conformation change between four-coordinated to six-coordinated. The reversible change of coordination configuration facilitates the self-healing process. The film can be healed at room temperature if the damaged films are pre-treated by dipping into methanol solvents. Such features are intriguing in self-healing materials and our materials can be useful as solvent detecting materials with prolonged lifetime.

This work was supported by the Major State Basic Research Development Program (Grant Nos. 2011CB808704, 2013CB922100, and 2011CB933300), and Doctoral Fund of Ministry of Education of China (20120091130002). We thank Prof. Zhenan Bao (Stanford University, USA) for the helpful discussions.

### Notes and references

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<sup>†</sup>Electronic Supplementary Information (ESI) available: Syntheses and characterization of polymers, and supplementary figures. See DOI: 10.1039/c000000x/

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