

## Synthesis of a diamine cross-linker containing Diels–Alder adducts to produce self-healing thermosetting epoxy polymer from a widely used epoxy monomer†

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Nan Bai,<sup>a</sup> Kei Saito<sup>\*b</sup> and George P. Simon<sup>\*a</sup>

A diamine cross-linker with thermal reversible Diels–Alder (DA) adducts of furan and maleimide groups has been designed and synthesised, which can be used to crosslink commercial epoxy monomers to achieve self-healing, cross-linked epoxy polymers. This new strategy to make self-healing epoxy polymer was successfully proved by incorporating the cross-linker with a widely used epoxy monomer, the diglycidyl ether of bisphenol A. The self-healing property of the new epoxy polymer was shown by complete elimination of cracks after the process of retro-DA and DA reactions which occurred in the cross-linker component of the network.

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### Introduction

In the past decades, self-healing polymers have become an exciting research field in the study of thermosetting polymers.<sup>1</sup> Irreversible damage, such as microcracks which can significantly reduce the load-carrying capacity properties of the materials and shorten their lifetime, can be healed.<sup>2–4</sup> For thermosetting materials (as compared to thermoplastic materials), self-healing is both challenging and important due to the fact that thermosets do not readily flow under the post-processing application of heat, as do thermoplastics.

To date, there are two main strategies to cause self-healing in thermosetting/cross-linked polymers: autonomous mending and external stimuli mending.<sup>4</sup> Autonomous mending is based on the incorporation of micro-containers or capsules which contain healing agents (monomers and/or catalysts) and are distributed throughout the cross-linked polymeric matrix. When damage occurs and a crack grows, it breaks the micro-containers, releasing the healing agents into the crack, the catalyst causing polymerization, and subsequent solidification and crack healing.<sup>5,6</sup> The other strategy achieves mending based on the use of external stimuli which are related to the chemical properties of the polymer, and rely on the appropriate application of external stimuli. At the point of polymer design, special functional groups are introduced into the polymer molecules, which can react to heal the cracks by external stimuli. This kind

of healing tends to be reversible and repeatable. The stimuli include heat and light,<sup>7</sup> but various functional groups can be designed to allow a wide range of stimuli to be used.<sup>1,3,4,8</sup> Wudl and co-workers successfully used Diels–Alder (DA) reaction/retro Diels–Alder (rDA) reaction strategy to produce self-healing polymers.<sup>2,9</sup> The highly cross-linked polymer synthesised from multifunctional furan and maleimide could heal the cracks after a heating and cooling process.

Epoxy resins have many applications in a range of fields, including fibre-reinforced plastic materials, potting materials for electronics, coatings, civil engineering applications and as general purpose adhesives,<sup>10,11</sup> many of which would be beneficial if they could be made repairable. Following Wudl's approach, Liu and Hsieh used epoxy compounds as precursors to simply synthesise trifunctional furan and maleimide.<sup>12</sup> The thermally remendable cross-linked polymer prepared from those monomers can be seen as a new kind of epoxy polymer and it can be healed via rDA and DA reactions. Tian *et al.* made a novel epoxy resin with a furan group in the structure.<sup>13</sup> After reacting with difunctional maleimide and being cured with anhydride, it formed a new cross-linked epoxy which can heal the cracks through chain reconnection resulting from rDA and DA reactions. In a subsequent paper, they changed the structure of epoxy resin and finally get a new self-healing epoxy with a higher self-healing efficiency.<sup>14</sup>

Previous works have only focused on modifying the epoxy monomer to contain the DA group.<sup>13,14</sup> Clearly this would be expensive to widely implement, and it would be desirable to be able to use common, commercially available epoxy monomers. In our research, a new strategy was researched, where the thermally reversible DA unit can be incorporated into the diamine cross-linker as the healable element. This has the advantage that it can be used for a range of different commercial epoxy monomers, including in the aerospace industry,

<sup>a</sup>Department of Materials Engineering, Monash University, Clayton, VIC 3800, Australia. E-mail: [george.simon@monash.edu](mailto:george.simon@monash.edu); Fax: +61 399054934; Tel: +61 399054936

<sup>b</sup>Centre for Green Chemistry, Monash University, Clayton, VIC 3800, Australia. E-mail: [kei.saito@monash.edu](mailto:kei.saito@monash.edu); Fax: +61 399058501; Tel: +61 399054600

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liquid. *Exo* and *endo* ratio of compound **4** was determined by  $^1\text{H}$  NMR as *exo/endo* = 6.7 : 1. *Exo* isomer:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.54 (d,  $J$  = 5.7 Hz, 2H), 6.50 (dd,  $J$  = 5.7, 1.6 Hz, 2H), 5.20 (d,  $J$  = 1.7 Hz, 2H), 3.43 (t,  $J$  = 8.0 Hz, 4H), 3.34–3.11 (m, 4H), 2.94 (d,  $J$  = 6.4 Hz, 2H), 2.83 (d,  $J$  = 6.4 Hz, 2H), 1.55–1.39 (m, 4H), 1.24 (s, 8H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  176.27, 175.36, 138.57, 137.08, 92.45, 91.97, 82.99, 80.80, 50.46, 48.06, 41.46, 39.74, 28.94, 27.59, 26.55. ESI-MS ( $m/z$ ):  $[\text{M} + \text{H}]^+$  calc. for  $\text{C}_{26}\text{H}_{35}\text{N}_4\text{O}_6$  499.3, found 499.1. FTIR  $\nu$  ( $\text{cm}^{-1}$ ) 3373, 2932, 2857, 1768, 1692, 1439, 1402, 1153, 731.

### Preparation of the cross-linked epoxy polymer

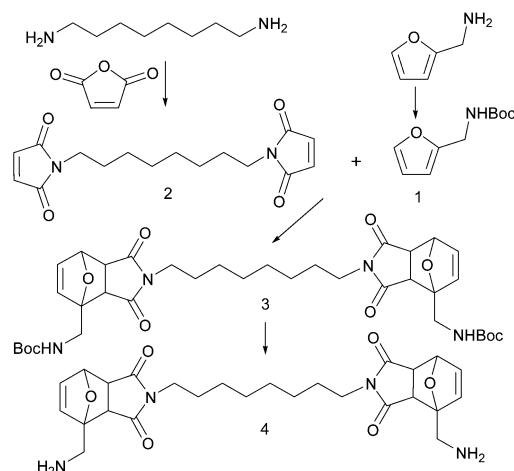
Diamine cross-linker (**4**) (1.21 g, 2.43 mmol) and DGEBA (1.8 g, 4.86 mmol) were mixed directly and degased under vacuum (0.5 mm Hg) for 3 hours. After that, the mixture was heated at  $60^\circ\text{C}$  for 10 hours to get the cross-linked epoxy polymer. FTIR  $\nu$  ( $\text{cm}^{-1}$ ) 3431, 2927, 2858, 1766, 1691, 1604, 1506, 1400, 1238, 1180, 1032, 827.

## Result and discussion

### Synthesis and characterization of the diamine cross-linker (**4**)

The diamine cross-linker (**4**) with DA adducts was synthesized.

Scheme 1 shows the synthesis process. The 1,8-diaminooctane reacted with maleic anhydride under the catalysis of acetic anhydride,  $\text{nick}(\text{II})$  acetate and triethylamine in refluxed acetone to obtain compound **2**.<sup>16</sup> Furfurylamine was protected by Boc group to get compound **1**. Compound **1** and **2** reacted in EtOAc to obtain compound **3** as a mixture of *exo* and *endo* isomers under reflux. After two Boc groups were deprotected and HCl salt was neutralized using NaOH solution, the final product compound **4** was successfully obtained. It was a very viscous liquid with brown colour and it is a mixture of *exo* and *endo* isomers as same as compound **3**. From the  $^1\text{H}$  NMR spectrum of compound **4**, the ratio of *exo/endo* is 6.7 : 1 and *exo* isomer is the main product.<sup>17–20</sup> However, the pure *exo* or *endo* isomer is not necessary for the self-healing epoxy polymer synthesis because both of the isomers undergo DA and rDA



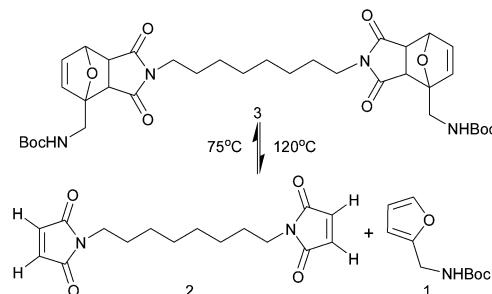
Scheme 1 Synthesis of diamine cross-linker (**4**) with two adducts.

reactions and thus serve the self-healing purpose. This is the first time this kind of diamine cross-linker (**4**) was synthesised and reported.

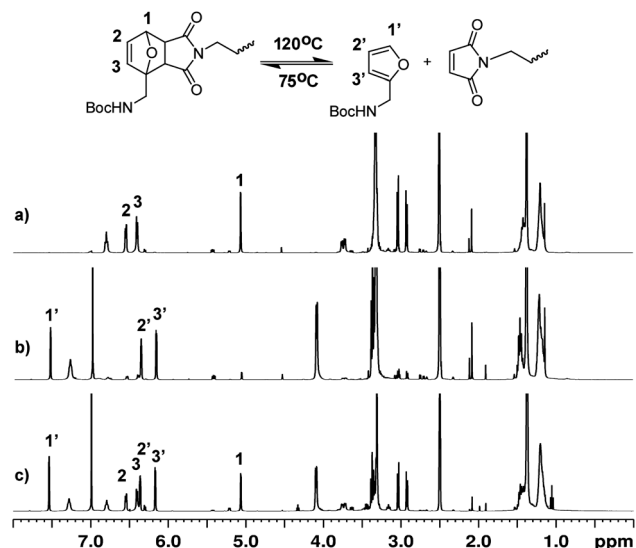
### DA and rDA reactions in the diamine cross-linker

In this research, two pairs of furan and maleimide groups as healable units were put into the diamine cross-linker (**4**) in order to make the final epoxy polymer have the self-healing property. DA and rDA reactions are the chemical foundation of self-healing properties, so it was necessary to confirm whether the diamine cross-linker has the cyclizing reaction ability of DA and rDA reactions. Since the final epoxy polymer is a cross-linked polymer and cannot be dissolved in any solvents, it was necessary to determine whether the DA and rDA reactions occurred in the diamine cross-linker itself at this stage because of its better solubility in organic solvents. According to the literature,<sup>13,14</sup> DA and rDA reaction temperatures of the current system were set at  $75^\circ\text{C}$  and  $120^\circ\text{C}$ .  $^1\text{H}$ -NMR was used to test the cycle of DA and rDA reactions. Pure diamine cross-linker (**4**) can not be exposed to these tests, because the  $\text{C}=\text{C}$  double bond in maleimide group readily reacts with the amine group when temperature is above  $70^\circ\text{C}$ , due to Michael Addition.<sup>21</sup> Upon the rDA reaction occurring, the amine group attacks the  $\text{C}=\text{C}$  double bond, which would stop the subsequent DA reaction. Thus, the Boc-protected diamine cross-linker (**3**) was used to do this test (Scheme 2).

In order to investigate the DA and rDA reactions of the cross-linker itself, a series of experiments with compound **3** were carried out. Compound **3** was added to a NMR tube in  $\text{DMSO-d}_6$ , which was selected as the solvent because of its high boiling point,  $189^\circ\text{C}$ . The  $^1\text{H}$ -NMR was first run at room temperature, and the sample was then heated at  $120^\circ\text{C}$  for 30 minutes and quenched quickly to room temperature before  $^1\text{H}$ -NMR test was run again. After that, the sample was treated at  $75^\circ\text{C}$  for 20 hours and cooled to room temperature and retested. The resultant spectra are shown in Fig. 1. Peaks of 1, 2 and 3 stood for the DA adduct, and peaks of 1', 2' and 3' ascribed to furan group in rDA product. Before heating, only peaks of 1, 2 and 3 were observed (Fig. 1a). After heating at  $120^\circ\text{C}$  for 30 minutes, peaks of 1, 2 and 3 disappeared and peaks of 1', 2' and 3' appeared (Fig. 1b). This showed the appearance of the furan groups and showed that the rDA reaction had occurred. The sample was then treated at  $75^\circ\text{C}$  for 20 hours, following which



Scheme 2 DA and rDA reactions in compound **3**.



**Fig. 1**  $^1\text{H}$  NMR spectra of cycle of DA and rDA reaction. (a) Before heating; (b) heated at  $120^\circ\text{C}$  for 30 minutes and quenched quickly to room temperature; (c) heated at  $120^\circ\text{C}$  for 30 minutes, then treated at  $75^\circ\text{C}$  for 20 hours and cooled to room temperature.

peaks of 1, 2 and 3 appeared once again (Fig. 1c), proving that adducts of furan and maleimide groups reformed and the DA reaction occurred. The test thus verified the cycling of DA and rDA reactions in the system. As the experiment was in a NMR tube, the solution was not able to be stirred and the concentration of the solution was also not very high, so it took some 20 hours to get a better NMR spectrum (Fig. 1c) to show DA reaction happened. It would be quicker inside the epoxy polymer.

### Preparation and characterization of the cross-linked epoxy polymer

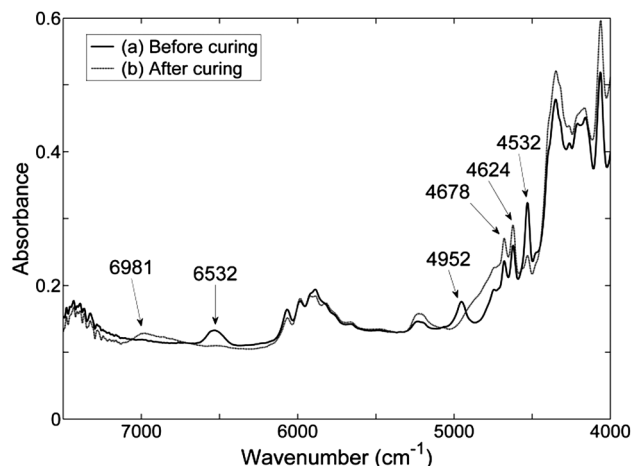
The cross-linked self-healing epoxy polymer was synthesised by step growth polymerisation of epoxide and amine groups. DGEBA was chosen as the epoxy monomer because it is a common, widely used epoxy monomer.

The compound **4** was mixed with DGEBA at room temperature and degassed using a vacuum oven. The molar ratio of NH groups and epoxide groups was 1 : 1. After that, it was heated at  $60^\circ\text{C}$  for 10 hours to get the final, self-healing epoxy thermosetting polymer (Scheme 3), which was found to be insoluble. Since one amine group can react with two epoxide groups, the diamine cross-linker is thus able to react with four epoxide groups to yield a cross-linked epoxy polymer.

Near infrared (NIR) spectroscopy can be used to monitor the reaction of the epoxy polymer formed, where peaks observed in Fig. 2 could be assigned on previous reports.<sup>22–24</sup> Since samples used had slightly different thicknesses, internal peak standards were used to compare different spectra. The peaks at  $4624$  and  $4678\text{ cm}^{-1}$  were from the phenyl group band, which did not change during the curing process and thus were a suitable internal standard. The spectrum of the uncured mixture of DGEBA and the diamine cross-linker (Fig. 2a) showed a strong peak at  $4532\text{ cm}^{-1}$  from the epoxide group and two peaks at  $4952$  and  $6532\text{ cm}^{-1}$  for the amine groups. After curing at  $60^\circ\text{C}$  for 10 hours, the peak at  $4532\text{ cm}^{-1}$  became very weak and the two peaks at  $4952$  and  $6532\text{ cm}^{-1}$  nearly disappeared (Fig. 2b), whilst simultaneously a peak at  $6981\text{ cm}^{-1}$  for the hydroxyl group appeared. These changes clearly showed that the curing reaction between epoxide and amine groups occurred, and



**Scheme 3** The curing reaction between the synthesised diamine cross-linker (**4**) and DGEBA.



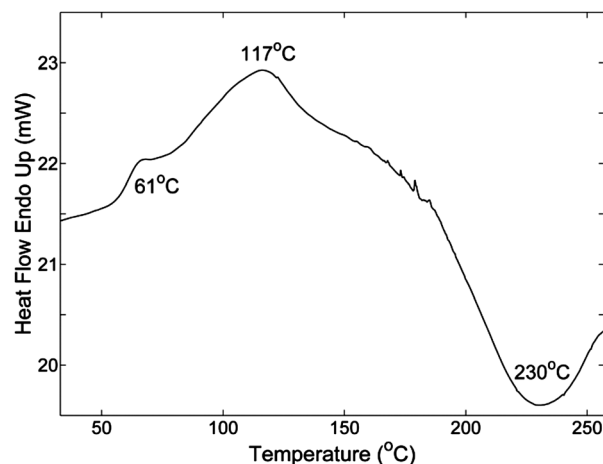
**Fig. 2** Near infrared spectra of (a) an unreacted mixture of DGEBA and the diamine cross-linker, and (b) a mixture of DGEBA and diamine cross-linker cured at 60 °C for 10 hours.



**Fig. 3** DSC result of a mixture of unreacted DGEBA and diamine cross-linker (4). Heating rate is 2 °C min<sup>-1</sup>.

hydroxyl group was produced as a result. Peak-fitting software (Igor Pro 6.2) was used to calculate the curing percentage by comparing the height of the epoxide group peak at 4532 cm<sup>-1</sup> to that of original uncured mixture, normalised by the internal standard, and the resultant cure was 79.8%.

In order to better understand the curing process, differential scanning calorimetry (DSC) was carried out on the reactive mixture. The DSC scan of the mixture of DGEBA and diamine cross-linker (4) was shown in Fig. 3. The DSC curve had two apparent exothermic peaks at 105 and 186 °C representing the curing reaction and an endothermic peak at 155 °C due to the rDA reaction. In order to better understand the 2nd peak at 186 °C, curing agent Ethacure 100 diamine was used to mix with DGEBA and the mixture was tested without curing. The DSC result was shown in Fig. S1 in the ESI.† The curing temperature range of the mixture of DGEBA and Ethacure 100 amine was from 100 °C to 250 °C. Because the diamine cross-linker (4) is less rigid than the Ethacure 100 diamine, the curing temperature



**Fig. 4** DSC result of the cured epoxy polymer reacted at 60 °C for 10 hours. Heating rate is 5 °C min<sup>-1</sup>.

range of the mixture of DGEBA and diamine cross-linker should be lower and the range from 50 °C to 200 °C is reasonable. It is clear that the curing reaction started from about 50 °C. When the temperature was above 105 °C, an endothermic peak appeared due to the rDA process occurring before the curing reaction finished, further heating shows a continued exotherm due to ongoing cure.

DSC was also used to obtain the  $T_g$  of the epoxy polymer, which was cured at 60 °C for 10 hours (Fig. 4). From the result,  $T_g$  was about 61 °C, which is lower than the temperature of rDA reaction (117 °C). The rDA peak in the uncured system appears at 155 °C (Fig. 3), but this is likely because it is the rDA peak combined with the curing reaction exothermic peak. Additional post curing was observed when the temperature was above 200 °C.

The cured cross-linked epoxy polymer sample was scanned by TGA (Fig. 5) showed that, the new self-healing epoxy polymer had 6% weight loss under 300 °C. When the temperature of the sample was above 140 °C, rDA reaction occurred and crosslink became partially cleaved, and the polymer effectively became a



**Fig. 5** TGA result of the cured cross-linked epoxy polymer.

liner polymer. Since the curing percentage of the sample was 79.8%, some proportion of the 20% unreacted epoxy monomers were likely thermally released *ca.* 6%, mostly likely due to epoxy monomer (as opposed to pendent unreacted groups), whilst some of the remaining material continued to cure. The weight reduced to 60% at about 370 °C due to the loss of its more volatile side organic group.<sup>25</sup> Cross-linked epoxy polymer cured with Ethacure 100 diamine, an aromatic amine without DA adducts, was also tested by TGA (Fig. S2 in the ESI†) for comparison and the degree of cure of that sample was 82.4% (preparation of the sample given in the ESI†). The weight loss was 2% under 300 °C, because the cross-like part cannot be broken and the uncured epoxy monomer cannot be released. Compared with result of the sample without DA adducts, the stability of sample with DA adducts was a little lower from 200 °C to 300 °C. However it shows that the cross-linker is stable throughout the temperature range of the healing process (shown shortly).

### DA and rDA reactions in the cross-linked epoxy polymer

When the cross-linked epoxy polymer was prepared, it was not able to be dissolved in any solvents. FTIR was found to be the best option to observe the DA and rDA reactions in the system. 140 °C was chosen as the temperature for breaking adducts and the results were good. Whilst cooling the sample down should allow the reformation of sufficient adducts, it was found that annealing at temperature of 75 °C was useful to cause fuller regeneration of the adducts. The peak at 694  $\text{cm}^{-1}$  is the peak of C–H bond attached the C=C in the maleimide ring (Scheme 2).<sup>26</sup> The height change of that peak was used to know the difference in the (forward) DA and (backward) rDA reactions. The maleimide carbonyl peak at 1691  $\text{cm}^{-1}$  was used as internal standard to allow quantification.<sup>26</sup> The results are shown in Fig. 6. After the cross-linked epoxy polymer sample was heated at 140 °C for 30 minutes and quenched quickly to room temperature. The peak at 694  $\text{cm}^{-1}$  then became bigger (Fig. 6b) compared to the original sample (Fig. 6a) due to the increasing amount of maleimide groups in the system after



**Fig. 6** FTIR spectra of (a) the cured epoxy polymer; (b) heated at 140 °C for 30 minutes and quenched quickly to room temperature; (c) after that, treated at 75 °C for 5 hours and cooled to room temperature.



**Fig. 7** Photos of (a) scratches made on the surface of the cross-linked epoxy polymer sample, (b) partially healed sample after heated at 140 °C for 3 minutes and (c) fully healed sample after heated at 140 °C for 30 minutes.

heating, and rDA reaction occurred to break adducts. The sample was then treated at 75 °C for 5 hours and cooled to room temperature. The peak at 694  $\text{cm}^{-1}$  was reduced in height (Fig. 6c), becoming similar to that of the original sample (Fig. 6a). This shows that the amount of maleimide groups decreased to a similar level as that of original sample, with the DA reaction reforming the adducts. The results showed that the heating/cooling cycle of DA and rDA reactions in the reacted epoxy polymer system worked well with the above healing condition. This cycle was repeated for 3 times, and similar results were obtained each time.

### Self-healing property of the cross-linked epoxy polymer

The self-healing property of the cross-linked epoxy polymer can clearly be seen in Fig. 7. A razor blade was used to make a flaw

on the sample surface (Fig. 7a), the crack being some 40 micrometres in width. The above condition for testing the DA and rDA reactions in the cured epoxy polymer was used. The sample was heated at 140 °C for 3 minutes and was partially healed. The crack width became smaller and was about 15 micrometres (Fig. 7b). After heated at 140 °C for 30 minutes, it can be clearly seen that scratches completely healed (disappeared) using an optical microscope (Fig. 7c). The fully healed sample was then heated at 75 °C for 5 hours to make it crosslink again. The round bubble inside the sample and the right edge of the sample helped to show that it was at the same position. According to the results of FTIR above (Fig. 6), DA and rDA reactions occurred in the epoxy polymer at these treatment temperatures, which helped to heal the cracks. Cross-linked epoxy polymer sample cured with Ethacure 100 diamine, which did not contain DA adduct, was used for comparison and the degree of cure of that sample was 82.4% (preparation of the sample given in the ESI†). The sample was subjected to the same conditions used to heal the polymers with the DA adducts (Fig. S3 in the ESI†). Although the crack became slightly less pronounced as a result of the enthalpy change during the heating process, it did not heal in the same way as the one with DA adducts did. The result showed that the epoxy polymer with the newly synthesised diamine cross-linker provided the expected self-healing behaviour. The same location on the polymer was used to be scratched and rehealed 3 times, indicating there was no “fatigue” or diminution of healing potential.

## Conclusions

A new strategy of making a self-healing epoxy polymer by incorporating a diamine cross-linker synthesised with thermal reversible DA adducts of furan and maleimide groups is reported. A widely used epoxy monomer, DGEBA, was cured using the synthesised diamine cross-linker (4). The DA and rDA reactions in the cross-linked system of epoxy polymer thus formed were shown using FTIR. It was found that scratches on the epoxy polymer disappeared after treatment at 140 °C for 30 minutes. With the crack disappearing in a visible sense after the 140 °C heating, whilst the post-heat at 75 °C was suitable for getting maximal re-joining of the two adducts. The self-healing process was repeated a number of times and no diminution of healing potential was apparent. Further work is being undertaken to examine the temperature-dependence and kinetics of the healing process, including the minimum time required to cause the scratches to be healed.

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