

# Light-Activated Healing of Metallosupramolecular Polymers

*Gina L. Fiore, Stuart J. Rowan, and Christoph Weder\**

\*Correspondence: Prof. Dr. C. Weder, Adolphe Merkle Institute, University of Fribourg, CH-1700 Fribourg, Switzerland, Tel: +41 26 300 9465 E-mail: [christoph.weder@unifr.ch](mailto:christoph.weder@unifr.ch)

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Polymers which can be healed after sustaining damage are attractive for many applications.<sup>[1,2]</sup> Several routes are being explored to create such materials.<sup>[3]</sup> The simplest tactic is to liquefy a damaged polymer by exposure to solvent or heat.<sup>[4]</sup> In this case, healing involves the steps of surface rearrangement, wetting, diffusion, and chain re-entanglement. However, since the rates of the last two steps are inversely proportional to the molecular weight, healing of conventional polymers is slow and inefficient.<sup>[4]</sup> This problem can be overcome by exploiting thermally reversible, covalent bonds<sup>[5]</sup> or non-covalent supramolecular motifs.<sup>[6,7]</sup> These allow one to temporarily reduce the polymer's molecular weight by shifting the equilibrium to the monomer side when needed. The resulting increase in chain mobility and decrease in viscosity promote healing capability, before the equilibrium is shifted back and the polymer is reformed.

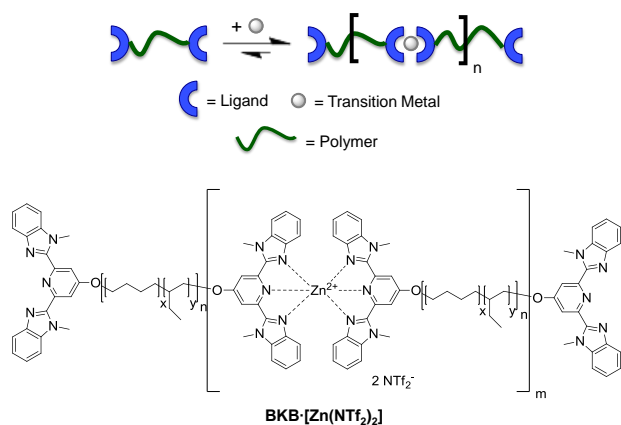
### Self-Healing Metallosupramolecular Polymers

Previous work in our group showed that the supramolecular assembly of telechelic ditopic ligands with transition metal salts affords metallopolymers that combine ease of processing and good mechanical properties.<sup>[8]</sup>

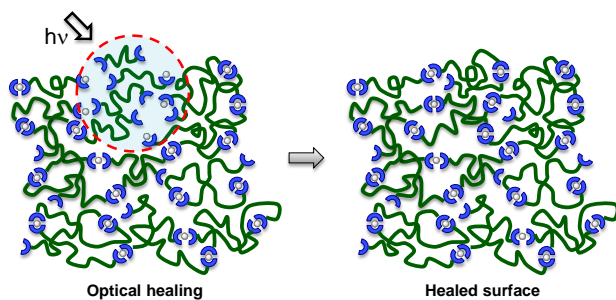
We recently employed this approach to create supramolecular materials in which defects can be healed upon exposure to light.<sup>[9]</sup> These materials consist of a telechelic poly(ethylene-*co*-butylene) macromonomer with 2,6-bis(1'-methylbenzimidazolyl)-pyridine ligand chain ends, which was polymerized with equimolar amounts of Zn(NTf<sub>2</sub>)<sub>2</sub> and La(NTf<sub>2</sub>)<sub>3</sub> (Figure 1). This resulted colourless elastic films which exhibit appreciable mechanical properties. Electron microscopy and X-ray diffraction experiments revealed a phase-separated, layered morphology (Figure 2), which is the origin of the materials' intriguing mechanical properties. Upon exposure to ultraviolet light, the metal-ligand motifs are excited and convert the absorbed energy into heat. This facilitates the temporary dissociation of the metal-ligand motifs (Figure 2) and transforms the polymer into a low-viscosity liquid, which can easily fill small defects. When the light is switched off the structures re-assemble and the original properties are restored.

An important aspect of the new approach is that light can be applied locally, so that objects can be healed under load. The general design, based on supramolecular polymers and a light-heat conversion step, can be applied to a wide range of supramolecular materials that use different chemistries.

- [1] S. D. Bergman, F. Wudl, *J. Mater. Chem.* **2008**, *18*, 41.
- [2] R. P. Wool, *Soft Matter* **2008**, *4*, 400.
- [3] E. B. Murphy, F. Wudl, *Prog. Polym. Sci.* **2010**, *35*, 223.
- [4] Y. H. Kim, R. P. Wool, *Macromolecules* **1983**, *16*, 1115.
- [5] X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nutt, K. Sheran, F. Wudl, *Science* **2002**, *295*, 1698.
- [6] A. W. Bosman, R. P. Sijbesma, E. W. Meijer, *Mater. Today* **2004**, *7*, 34.
- [7] P. Cordier, F. Tournilhac, C. Soulie-Ziakovic, L. Leibler, *Nature* **2008**, *451*, 977.
- [8] a) D. Knapton, S. J. Rowan, C. Weder, *Macromolecules* **2006**, *39*, 651. b) D. Knapton, P. K. Iyer, S. J. Rowan, C. Weder, *Macromolecules* **2006**, *39*, 4069. c) M. Burnworth, J. D. Mendez, M. Schroeter, S. J. Rowan, C. Weder, *Macromolecules* **2008**, *41*, 2157.
- [9] 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.



**Figure 1.** Schematic of the supramolecular polymerization of ligand-terminated macromonomers with metal salts and chemical structure of some of the light-healable metallosupramolecular polymers studied



**Figure 2.** Schematic representation of the light-activated healing of metallosupramolecular polymers.