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COMMUNICATION

A Facile Approach to UV/Heat Dual-Responsive Triple Shape Memory Polymer

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In the present work, a facile approach was employed to fabricate UV/heat dual-responsive triple shape memory polymer (SMP) by simply mixing $Zn(Mebip)_2(NTf_2)_2$, a metallosupramolecular unit formed by coordinate 2,6-bis(N-methyl benzimidazolyl)-pyridine (Mebip) ligands to Zinc di[bis(trifluoromethylsulfonyl)-imide] ($Zn(NTf_2)_2$), into one part of epoxy resin. Dissimilar to previously reported UV sensitive SMPs with sophisticated molecular structure and relative poor mechanical properties, the advantage of this approach is that the UV-sensitivity was simply achieved by employing $Zn(Mebip)_2(NTf_2)_2$, a UV-Heat transfer compound,[1] into the polymer matrix without significant sacrifice of thermal and mechanical properties. Also thanks to the light-heat transfer nature of $Zn(Mebip)_2(NTf_2)_2$ and segmented material structure, the outcome polymer displayed UV sensitivity to composite part, while leaving the shape of neat SMP part unchanged under UV source (solely thermal sensitive). Thus the outcome composite displayed excellent UV and heat selective localized triple shape memory effect.

Shape memory polymers (SMPs) are a class of stimuli-responsive materials which are able to revert to the pre-defined shape upon a stimulus.[2,3] Traditional SMPs are generally realized by introducing net-points into a polymer with proper phase transition temperature (T_{trans}), forming thermal induced one-way dual-shape memory polymers (1WDSMPs).[4] The net-points determine the permanent shape, while the rest polymer act as switch to immobilize the temporary shape. A typical programming cycle for 1WDSMPs consists of four steps. First, the SMP was heated above its T_{trans}. Then the SMP was deformed and fixed by external force. Then the fixed SMP was cooling down (below the T_{trans}) and release the

external force, the network will reach to a thermodynamic unstable while dynamic stable state. (so called temporary shape) Finally, the SMP was heated above its transition temperature, the switch is on (the mobility of the polymer will increase) and network will reach to a dynamic and thermodynamic stable state (so called permanent shape).[5,6]

The SMP which could also memorize 2 temporary shapes and realize shape changing among three shapes, were called triple shape memory polymers (3SMPs).[7-9] Typically the 3SMPs were realized by introducing additional switches (either chemically or physically) into a normal 1WDSMP net-work, which could be a polymeric switch[10-12]/network[13] with distinct T_{trans}, self-complementary hydrogen bonding moieties,[14] or even utilize the two phase change in crystalline type switch (for example, PCL[13]). These unique abilities of 1WDSMPs and 3SMPs have been utilized for a number of applications in biomedical, packaging, textile and aerospace areas.[3,15,16]

Despite commonly utilized direct heating, other alternative triggering mechanisms like light and magnetic fields have also been developed.[17] These methods enabled remote triggering of shape recovery and make SMPs more feasible in vivo applications. In previous demonstrated light-induced shape memory system,[18] light-sensitive components such as gold nanoparticle (responsive to laser in visible light region), graphene oxide (responsive to infrared light region), organo-metal compound and cinnamic groups (responsive to UV region) were embraced into polymer network either covalently or non-covalently to realize such purpose. Zhao et al. introduced functionalized AuNPs into the biodegradable SMPs to realize the

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visible light triggered shape recovery.[19,20] Rowan et al reported a covalently cross-linked metallosupramolecular shape memory polymers with metal salt and poly(butadiene) which was end-capped with Mebip.[1,21] The key component in fixing and releasing the temporary shape is the UV induced heating effect on metal-ligand units that lead to their dissociation-association. This mechanism was previously proved by Weder et al[1] for fabricating UV-induced self-healing, where new bonding could be reversibly formed among the neighbor fracture surfaces. For SMPs with cinnamic groups, their SME are realized by reversibly photo fixing (r>260nm) and photo cleaving (λ <260nm) of cinnamic groups.[22] Although polymers with cinnamic groups and -OMebip are UV responsive, they are covalently connected to the polymers to realize light sensitivity. Therefore, compare to other commercial polymers like epoxy resin and polyurethane, the polymers mentioned above are difficult to fabricate and their mechanical properties are relatively poor. Compared to tuning molecular structures, blending light-heat transfer components into original polymer matrix is better because they are easy to process and maintain (even enhance) the original mechanical performance of the matrix. However, to the best of our knowledge, so far there's few report on the UV-sensitive SMPs with composite approach.

Figure 1. A) illustration of composition of SMP, shape recovery routes (from shape #1 to the permanent shape). B) molecular structure of $Zn(Mebip)_2(NTf_2)_2$. C) differential scanning calorimetry of the second heating curve of each parts of the SMP. D) temperature-time relationship of the each region under UV irradiation.

Driven by increasing sophisticated demand of materials and devices, developing SMPs with additional functions like dual-responsiveness[8] are fueled by technological needs.[23,24] Here, we report a triple shape memory polymer composite featuring both remote triggering of the shapes recovery with UV source and heat. Our approach for light-sensitive is based on the principle that the $Zn(Mebip)_2(NTf_2)_2$, as shown in Figure 1B, can transfer UV source into heat.[1] Mebip and related Zinc complex were synthesized according to literature with slight modification.[1,25,26] Epoxy resin was chosen as the matrix because of its facile synthesis routine, tunable transition temperature at different region and great mechanical property (for example, high recovery force[27]). The shape memory behavior of epoxy resin has been investigated elsewhere.[28] The bi-responsive shape SMPs in present work was realized by casting the $Zn(Mebip)_2(NTf_2)_2$ embedded epoxy pre-polymer to the surface of pre-cured neat epoxy resin. Such a conceptual material design was shown in Figure 1A. The target SMP consist of two regions: the $Zn(Mebip)_2(NTf_2)_2$-SMP (right region) and neat SMP. The permanent straight shape was first deformed into the shape 1, in which strains were introduced into each region. For shape 1, the recovery of the $Zn(Mebip)_2(NTf_2)_2$-SMP region can be remotely actuated by the UV source without enacting the recovery of the other region. As such, after UV irradiation, it could recover to the permanent shape by heating. Since the approach relies on selective localized actuations, a broad shape memory transition or two distinct shape memory transitions, which are required for other known triple shape memory polymers, are not needed here.
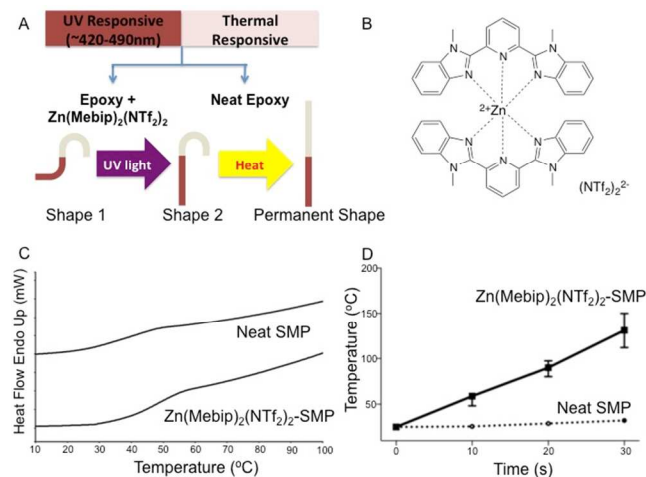
Detailed raw materials for synthesis and characterization method are available in supplemental information. (SI) The molar ratio of the liquid epoxy precursor for the SMP samples was E-51/NGDE/Jeffamine (D230) = 2:1:3 because, according to our previous experience, the T_g of the outcome polymer with this recipe is in body temperature region. Weighted nanoparticles (0.2g bulk $Zn(Mebip)_2(NTf_2)_2$ which was solved in CH_2Cl_2/MeCN) were dispersed into the mixture of E51(1.0g) and NGDE(0.3g), then the solvent was removed under vacuum. The nanoparticles was further dispersed by ultrasonication for 10 mins. Next, Jeffamine (0.47g) was added into the dispersion. The obtained mixture was further mixed mechanically for 30s before cured. Inspired by Xie's work,[17] the SMP was synthesized in two steps. First, the neat SMP monomer solution, a mixture with E51 (2.5g), NGDE (0.7g) and Jeffamine (1.1g), was partially cured for 60 mins at 80°C in a 7.5cm×2.5cm

Teflon mold. Then, the neat SMP was evenly cut into 2 pieces in the long axis and leave the right part in the mold. (the left side were left blank) Finally, the Zn(Mebip)$_2$-SMP monomer solution were casted into the related blank part of the mold and fully cured. The overall measurement of the demonstration sample is 75mm×2mm×1mm. Two regions are both around 37mm in length. The mass ratio of Zn(Mebip)$_2$(NTf$_2$)$_2$ was 10%.

Generally, the value of T$_{trans}$ is important as it determined the application area of the outcome polymer.[29,30] For example, a T$_{trans}$ close to (usually slightly below) 37°C is preferred for biomedical applications,[31] while a high T$_{trans}$ (say, 100°C) is required for aerospace applications[16]. Either dynamic mechanical analysis (DMA) or differential scanning calorimetry (DSC) can be employed to study the T$_{trans}$. In our work, the T$_{trans}$ of the outcome SMPs were evaluated by DSC with a scanning rate of 10°C/min. As the material is with two parts (neat SMP and composite SMP), their T$_{trans}$ were studied separately. As shown in Figure 1$_C$ (the 2nd heating curve of the sample, as the first heat curve is to eliminate thermal history), the phase change of two parts are in glass transition nature and their glass transition temperatures (T$_g$) are close to or slightly higher than body temperature. For neat SMP, a apparent T$_g$ was found at 37°C, while the T$_g$ of Zn(Mebip)$_2$(NTf$_2$)$_2$-SMP is slightly shifted to 48°C. This phenomenon may be caused by the rigid nature of the organo-metal additives which hindered the mobility of the molecular chain. This result suggested that the T$_{trans}$ of both part are close to body temperature. The T$_g$ of Zn(Mebip)$_2$(NTf$_2$)$_2$-SMP could be further tuned to body temperature by slightly increase the ratio of NGDE in matrix.

The pre-requirement of triple shape memory effect with two types of stimuli is that, at least one part of the sample is selectively respondent to a stimuli while the other part is less affected under the same stimuli. In our case, we anticipated that the Zn(Mebip)$_2$(NTf$_2$)$_2$-SMP should be sensitive to both UV and heat while the neat SMP part is solely thermal responsive. To prove the selective activation of the sample under UV source, the temperature-time relationship of each region (neat SMP part and composite part) was conducted. The UV source was generated from SunSpot SM 2 from Shenzhen Wisbay M&E Co., LTD. The sample surface temperature during heating was recorded with IR camera. As shown in Figure 1$_D$, the temperature of Zn(Mebip)$_2$(NTf$_2$)$_2$-SMP part rapidly increased above their transition temperature after 10 seconds while the temperature of neat SMP part maintained below its

transition temperature. This indicate that the Zn(Mebip)$_2$(NTf$_2$)$_2$ is an efficient light-heat transfer agent. The light-heat transfer mechanism has been reported elsewhere.[1] Besides, the slight of temperature increase from neat SMP may be caused by the heat effect from the UV source, but such heat effect is not high enough to trigger the shape recovery of the neat SMP part.
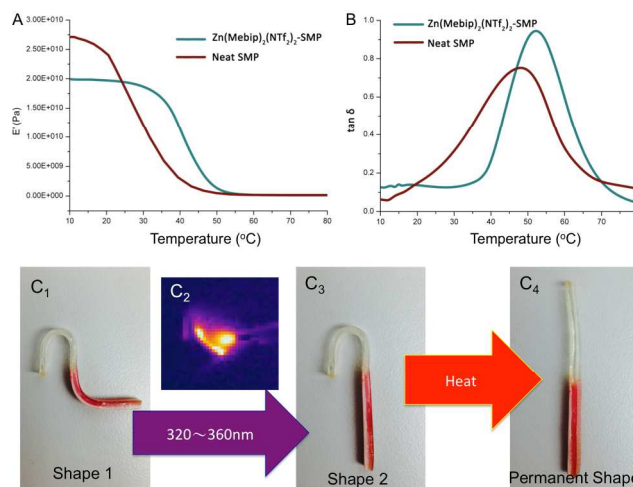

Figure 2. Dynamic mechanical analysis and demonstration of triple-shape effect. (A) and (B) illustrated the elastic modulus and tan δ of each SMP part. The deformed sample (C$_1$) was exposed to UV source and heat sequentially, leading to temporary shape 2 (C$_3$) and permanent shape (C$_4$). C$_2$ is the IR image taken by a FLIR E55 IR camera from above of the sample when it was exposing to UV source.

The mechanical properties of the SMPs were further studied by dynamic mechanical analysis (DMA) on a PerkinElmer DMA 8000 with bending method and the heating rate is 2°C/min. As shown in Figure 2A and 2B, the elastic modulus of neat-SMP and Zn(Mebip)$_2$(NTf$_2$)$_2$-SMP below the T$_g$ are around 2.0×10^4 MPa and 2.7×10^4 M, while decreasing to 1.3×10^4 MPa and 1.6×10^2 MPa above T$_g$ separately. The T$_g$s determined by tan δ are slightly higher than ones determined by DSC. The shape memory effect of the sample was conducted by bending test with angle as recover factor.[17,32] Shape fixity (R$_f$) and shape recovery (R$_r$) were evaluated by comparing the bending angle, fixed angle, and recovered angle. Samples were heated at 80°C and bend to 180° (bending angle) and then quenched in ice water for 1 min. The fixed angle was measured before the samples afterwards. The each region of the sample was then exposed to UV and subsequently heat. The final angle was

measured as the recovered angle. The shape fixity and shape recovery ratio of each part are all close to 100%. Furthermore, a demonstration was made to illustrate the UV/Heat sensitive triple shape memory effect. As shown in Figure 2, the sample was first deformed into a "s" shape #1, upon exposure to 320~360nm UV source which was applied by a horizontally fixed optical fiber, as shown in C_2, IR image suggested the selected activation of the $Zn(Mebip)_2(NTf_2)_2$-SMP part while neat SMP part maintain the original temperature. After 15 seconds' UV irradiation, the SMP change to shape #2, which was subsequently recovered to its permanent shape by immersing the SMP into hot water with $60^{o}C$.
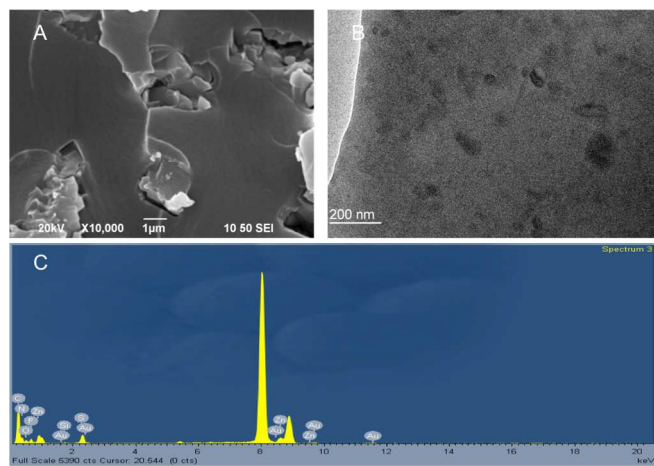

Figure 3. SEM, TEM and EDX images of the SMP composites. A) SEM image of $Zn(Mebimpy)_2(NTf_2)_2$-SMP at ×10000 magnification. B) TEM image of $Zn(Mebimpy)_2(NTf_2)_2$-SMP C) EDX image of composite.

The nanoparticulate dispersion and morphologies of the SMP composites were further characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 3_A, the fracture surface of the epoxy is relatively rough at low magnification of SEM. This may be caused by imperfect compatibility of epoxy matrix and the $Zn(Mebip)_2(NTf_2)_2$. Although some projections may be regarded as $Zn(Mebip)_2(NTf_2)_2$ clusters, unlike carbon nanotubes, they didn't display specific microstructure. Thus their dispersion can not be proved by simply SEM. To further study the dispersion of $Zn(Mebip)_2(NTf_2)_2$ in epoxy matrix, the TEM was employed as the Zinc is the only heavy element available in the composite system. As shown in Figure 3_B, the dark spots, which may be considered as Zinc, are dispersed relatively normally in the polymer matrix at high magnification. The

energy-dispersive X-ray spectroscopy (EDX) (Figure 3_C) further supported the existence of Zn in the matrix. The TEM proved that the $Zn(Mebip)_2(NTf_2)_2$ can be dispersed relative normally at high magnification. The compatibility may be further improved by modify the *p*-C on the pyridine with additional aliphatic branch.
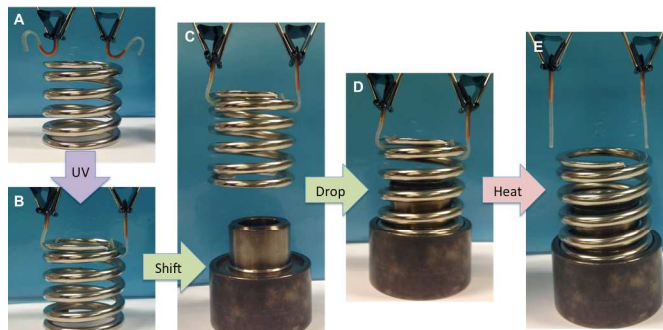

Figure 4. The demonstration of a practical application of the outcome SMP as robot hands.

One practical application was demonstrated by employing SMP as robot hands. As shown in Figure 4, A) initial state of robot hand was fabricated into *S* shape and exposed to UV source, resulting that B) the metal spring was hold by SMP. C) Then the spring was shifted above the metal base and D) installed on the base. E) The robot hands were further released by heat.

In summary, this work concerns a facile approach to UV/heat dual-responsive triple shape memory polymer. The molecular strategy of fabricating such polymer composite was realized by mixing $Zn(Mebip)_2(NTf_2)_2$ partially into epoxy resin (10wt%). Unlike other reported UV-sensitive SMP where a sophisticated polymer structure is required and which displayed relatively poor mechanical properties, the advantage of this approach is that UV-sensitivity can be simply introduced to SMP by simply employing $Zn(Mebip)_2(NTf_2)_2$ into any polymer matrix without significant sacrifice of thermal and mechanical properties. Also thanks to the light-heat transfer nature from $Zn(Mebip)_2(NTf_2)_2$ segmented material structure, the outcome polymer displayed UV sensitivity to composite part, while leaving the shape of neat SMP part unchanged. Thus the outcome composite displayed excellent UV and heat selective localized triple shape memory effect.

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Notes and References

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