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J. Am. Chem. Soc., Just Accepted Manuscript • Publication Date (Web): 24 Jan 2019 Downloaded from http://pubs.acs.org on January 24, 2019

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Multicolor Mechanochromism of a Polymer/Silica Composite with Dual Distinct Mechanophores

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Supporting Information Placeholder

ABSTRACT: The development of a multicolor mechanochromic polymer/silica composite is achieved by using two distinct types of mechanochromophores. The multicolor mechanochromism of the composite containing diarylbibenzofuranone (DABBF) in silicarich domains and naphthopyran (NP) in the polymer-rich domain is observed. The obtained composite shows blue, green, and orange colors according to the intensity of applied mechanical stimuli, solvent addition, and lapse of time. This unique multicolor mechanochromic behavior is evaluated by solid-state UV-vis absorption spectroscopy, ab initio steered molecular dynamics simulations, and computed minimum energy paths on force-modified potential energy surfaces. The unique mechanochromism is attributed to the difference in properties, activated colors, and domain locations between the two mechanochromophores.

Mechanochromic materials change color change when mechanical stimuli are applied, which can be utilized for stress detection and failure monitoring and prevention.¹ If the materials exhibit multicolor mechanochromism (mechanochromic properties showing two or more color changes in response to types or intensity of applied mechanical force), they can be utilized for multimodal analysis of material destruction and stress sensing. Several multicolor mechanochromic systems have been developed so far, including structural color,² supramolecular systems,³⁻⁵ and combination of spiropyran and pyrene⁶ or combination of rhodamine and pyrene.⁷⁻⁹ Introducing a mechanochromophore, i.e., a color-changing mechanophore,¹⁰ into polymers is one of the most effective approaches for obtaining mechanochromic materials. When mechanical force is



Figure 1. (a) Chemical structures of DABBF, NP, and their activated states. (b) Reverting behavior from the two activated states.

to a mechanochromophore-linked polymer, the mechanochromophore in the polymer chain is activated, which results in a color change of the material. Several types of mechanochromophores showing different colors with different mechanisms have been reported.¹¹⁻²⁹

However, most of them display a simple color change between two colors upon exposure to the mechanical stimulus and rarely display multicolor change except for the three-point anchored rhodamine mechanophore.³⁰ Since there are many mechanochromophore molecules reported, combining of mechanochromophores is a very approach useful for designing multicolor mechanochromic materials. However, reports on with polymer-based materials multiple mechanochromophores are very limited, given that rational molecular design of mechanophore systems is still challenging. Recently, we developed a polymerbased material exhibiting multicolor mechanochromism by using two radical-type mechanochromophores.³¹ A characteristic of radical-type mechanophores is their mechano-sensitivity to the mobility in polymer domains because they are in equilibrium with the corresponding dissociated colored-radical species. Dissociated radicals quickly recombine in high-mobility domains, resulting in no detectable color change or fast color fading. Therefore, their combination with other mechanophores whose mechanochromic properties are insensitive to mobility is expected to greatly contribute to the development of a wide variety of multicolor mechanochromic materials and to create their synergy effect.

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To demonstrate multicolor mechanochromism based on the combination of a dividing radical-type and another type of mechanochromophore, we focused on a polymer/silica composite as the matrix since it has both the soft domain of the polymer and the hard domain of the silica. The rigid framework of the silica hard domain, especially the interface between the hard and soft domains, maximize radical-type mechanophore performance because of their moderately limited mobility.³² Furthermore, the mechanical properties of the polymer/silica composite can be tuned by simply changing feed ratios of their precursors.

Here, we report a vivid three-color changing mechanoresponsive polymer/silica composite based on mechanistically distinct two types of mechanochromophores with different properties. We chose diarylbibenzofuranone (DABBF) as the dividing radical-type mechanophore and naphthopyran (NP) as the non-dividing isomerization-type mechanophore. As shown in Figure 1(a), the central C-C bond in DABBF is mechanically cleavable to generate the corresponding blue-colored arylbenzofuranone (ABF) radicals,³²⁻³⁸ and NP can be mechanically converted to the orange-colored merocyanine (MC) form by isomerization.¹⁴ The mixture of blue and orange activated species is expected to show a green color. Furthermore, the colored activated species have different absorbance peaks (λ_{max}) in the visible region; *i.e.*, the λ_{max} values of ABF radicals are 550 and 650 nm, and the λ_{max} value of MC is 440 nm, indicating that they can be distinguished by UV-vis

absorption spectroscopy. The most important feature of the combination is that they have significantly different reverting properties: ABF radicals cleaved from DABBF recombine very quickly in high-mobility regions such as in a low-glass transition temperature (T_g) polymer matrix in the bulk state, or in a solvent-swollen polymer matrix.³²⁻³⁸ On the other hand, MC, which can be reverted back to the NP state by visible light irradiation, has a somewhat long life time and is detected visually even in a high-mobility environment low- T_g polymer matrix;¹⁴ MC is able to retain its colored state even in a solvent-swollen polymer matrix (Figure 1(b)).



Figure 2. Synthesis scheme of the composite, an optical photograph of a sample piece, a TEM image, and illustration of the two mechanophores' locations in the sample.

As shown in Figure 2, the composite containing DABBF units at the interface and NP units at the polymer domain (**DABBF-NP Composite**) was prepared from DABBF alkoxysilane derivative (1) and poly(butyl acrylate) with dimethoxymethylsilyl groups at both chain ends and NP at the center of polymer chain (2) by using a sol-gel method as reported in our previous paper.³² The obtained sample was a pale-yellow film, and its morphology was observed by transmission electron microscopy (TEM). Both spherical silica



Figure 3. (a) Optical photographs and plausible illustrations showing mechanochromophores' activation states in the pristine, gently kneaded, strongly kneaded, and dichloromethane–added samples, and the sample left under visible light for 20 min after dichloromethane addition, and (b) their solid-state absorbance spectra. (c) Optical photographs and plausible illustrations showing mechanochromophores' activation states in the pristine and strongly kneaded samples, and the sample left under visible light after strong kneading for 30 min and 24 h, and (d) their solid-state absorbance spectra. The absorbance spectra were normalized by the absorbance intensity at 800 nm.

previous report.32

To investigate the mechanochromic behavior of the obtained composite, the DABBF-NP composite was kneaded gently in a mortar. Immediately, its color changed from pale vellow to blue, indicating as expected that DABBF units were activated (Figure 3(a) (1)–(2)). This is confirmed by the change in the solidstate UV-vis spectra before and after gentle kneading. An increase in the absorption peak intensities at 550 and 650 nm originating from ABF radicals was observed (Figure 3(b)(1)-(2)). With further strong kneading, the color of the composite changed to green due to the activation of NP units (Figure 3(a) (2)–(3)) with the increase in the absorbance around not only 550 and 650 nm, but also around 440 nm, which is attributed to the absorbance of MC (Figure 3(b) (2)-(3)). These phenomena indicate that DABBF units at the interface of the silica-rich domain were activated first, followed by the activation of NP in the polymer domain.

To gain a better understanding of the competing mechanochemical processes of DABBF and NP isomerization, we performed *ab initio* steered molecular dynamics (AISMD) simulations and computed minimum energy paths (MEP) on force-modified potential energy surfaces (FMPES)^{29, 39-40} of these two species. External forces of equal magnitudes were applied to the terminal atoms (Figure 4). The directions of the two force vectors were kept collinear to remove translational and rotational components of the forces. The electronic component of the potential energy surfaces was computed at UB3LYP level of theory with 6-31g* basis set (Details of the computational setup are described in SI). Firstly, to identify the reaction mechanochemical mechanisms under conditions. AISMD simulations were performed under external driving forces for both DABBF and NP. Under sufficient force, DABBF undergoes ultrafast fission to yield a pair of radicals on the picosecond timescale. At 3 nN, all 10 AISMD trajectories resulted in bond fission forming a pair of ABF radicals. Four possible *cis/trans* isomers exist for the MC product resulting from NP isomerization. Although these conversion pathways exhibit significantly different barriers without force, all four pathways were found to be feasible under load (SI). After 12 ps simulation at 3 nN, out of 10 AISMD trajectories, 6 gave double bond *cis-trans* isomer, whereas the other 4 were nonreactive. The cis-trans isomer is the main product at picosecond time scale. The product geometries obtained from AISMD at high forces and the geometries of NP and DABBF were optimized at forces ranging from 0 to 3 nN. Using these geometries as end points, minimum energy paths (MEP) were optimized. Enthalpy barriers obtained from these MEPs are plotted in Figure 5.

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Figure 4. Geometry and external force alignment for (a) DABBF, (b) pair of ABF radicals, (c) NP, and (d) MC (*cis-trans* isomer).



Figure 5. DABBF and NP reaction barriers on FMPES.

Although the barrier for bond fission in DABBF is significantly lower than that of NP in the absence of applied forces, the DABBF/NP bond fission reaction barriers become more similar with increasing external force. At an external force of 1.5 nN, the reaction barriers are 8.3 kcal/mol for DABBF and 15.1 kcal/mol

for NP. Although the bond fission reaction barrier for DABBF is slightly lower than that of NP, rapid mechanochemical transformations are expected for both species at the 1.5 nN force level which is easily achieved under kneading conditions. The low force magnitude needed for the reactions to take place and the small difference between the barriers of the two species suggest that there may be a little influence of the barrier differences in internal force distributions in the material domains are the more likely cause for the sequential activation of DABBF and NP.

Additionally, the composite was treated with a swellable organic solvent. After adding dichloromethane (DCM) to the strongly kneaded green colored sample, the composite was swollen and its color immediately changed to orange, indicating the recombination of ABF radicals at the interface (Figure 3(a) (3)-(4)). In the solid-state UV-vis absorbance spectra, the absorption peaks at 550 and 650 nm disappeared while the absorbance around 440 nm remained almost unchanged (Figure 3(b)(3)–(4)). Then, after 20 min under ambient light, the orange color faded, indicating that MC reverted to the NP state (Figure 3(a) (4)–(5)). In the solid-state UV-vis spectra, the absorbance around 440 nm disappeared (Figure 3(b)(4)-(5)). These phenomena indicated that solvent addition induces rapid recombination of ABF radicals; however, the reversion from MC to NP is relatively slow.

The composite captures its stress history. Materials that report both the peak load and load history provide a mechano-sensor capable of mechanochemical history recording. After 30 min under ambient light without any solvent, a strongly kneaded green sample changed to blue, which is caused by the reversion of MC to NP (Figure 3(c) (2)–(3)). This is supported not only by visual confirmation but also by the disappearance of the absorbance around 440 nm (Figure 3(d) (2)-(3)). Then, the blue color slowly faded due to the recombination of ABF radicals (Figure 3(c) (3) \sim (4)). In the solid-state UV-vis spectra, the intensity of the absorption peaks at 550 and 650 nm decreased slowly (Figure 3(d)(3)-(4)). These bulk observation indicates that the recombination of ABF radicals is slow in the low-mobility silica-rich interface because it is highly affected by molecular mobility. As a result, MC showed relatively fast reversion to NP.

In summary, we have demonstrated the multicolor mechanochromism of the polymer/silica composite with dual distinct mechanochromophores introduced into different domains, *i.e.*, a dividing type blue colorshowing DABBF mechanochromophore at mobility limited interface and non-dividing type orange colorshowing NP mechanochromophore in the soft domain. The composite showed blue, green, and orange color according to the strength of the mechanical stimuli,

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solvent addition, and lapse of time owing to the differences in mechanoresponsivity, reversion reaction, and domain location between the two mechanochoromophores. The present approach can be utilized for developing more sophisticated mechanochromic and mechanoresponsive soft materials.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

Synthesis and characterization data; details on NMR, IR, AISMD simulations, and MEPs.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

The authors thank Mr. Ryohei Kikuchi, National University Corporation Tokyo Institute of Technology Center for Ascended Materials Analysis, for the TEM measurements, Dr. Maxwell J. Robb and Ms. Abigail J. Halmes for their advice on the synthesis. This work was supported by KAKENHI grant 17H01205 (H.O.) from the Japan Society for the Promotion of Science (JSPS). T.K. acknowledges the financial support for JSPS Research Fellowships for Young Scientists (No.16J07264). V.M.L. thanks the Arnold and Mabel Foundation for Beckman а Beckman-Brown Interdisciplinary Postdoctoral Fellowship. T.J.M. and X.Z. acknowledge supported by the Office of Naval Research through the MURI on Photomechanical Material Systems (ONR N00014-18-1-2624).

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