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Non-symmetric Mechanophores Prepared from Radical-type Symmetric Mechanophores: Bespoke Mechanofunctional Polymers

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An non-symmetric radical-type mechanophore (CF/ABF) was synthesized by the molecular crossing between two radical-type mechanophores. Thermal stability and mechanoresponsiveness of CF/ABF were found to be tunable by the properties of parent RMs. CF/ABF-centred polymers showed mixed mechanochromism derived from simultaneous generation of two radical species.

Mechanochromic polymers, which can change colour in response to mechanical stress, have attracted great attention in the field of materials science as they allow visualizing stress and damage in materials.^{1–17} The incorporation of mechanophores (mechanochromophores) into polymers has been reported to enhance their mechanoresponsiveness.¹ A variety of mechanochromophores has been reported in this decade, including ring-opening-type mechanochromophores (e.g., spiropyran, naphthopyran,⁵ and rhodamine⁶) and radical-type mechanochromophores (RMs) such as dioxetane,² hexaarylbiimidazole,³ and diarylbibenzofuranone (DABBF).⁴ Recently, the extension of mechanochromophores to systems that exhibit multifunctional responses has become a research focus. For example, Robb et al. have reported force-dependent multicolour mechanochromism from a single mechanophore via a stepwise activation mechanism,¹⁸ while our group has achieved multicolour mechanochromism by mixing different mechanochromophores embedded in different polymer systems.^{20,21}

In this paper, we propose a novel approach to achieving multifunctional responses based on the hybridization of two different RMs. RMs exist in an equilibrium between the covalent species and the corresponding radical species, which can be shifted to the radical side by mechanical stress. We thus

considered establishing a radical exchange equilibrium between two different RMs and isolating the resulting hybridized RM as a potential method to achieve multifunctional responses. If different radicals were generated simultaneously in response to mechanical stimuli, a novel multifunctional system based on the functionality derived from each radical species could be developed.

As an example, the control of Se–S binding using light in a dynamic covalent binding unit that generates stable heterologous radical species has been reported by Xu et al.^{22,23} In this work, a non-symmetric molecular design is proposed based on RMs that generate different radical species simultaneously, which allows a variety of molecular functions to be derived from the parent RMs and expands the possibilities of RMs.

Typically, non-symmetric RMs cannot be isolated due to the radical exchange equilibrium between the two parent RMs at room temperature (e.g., DABBF; **Fig. 1a**). Recently, we developed difluorenylsuccinonitrile (DFSN),²⁴ a radical-type mechanochromophore that exhibits good thermal stability even at 80 °C (“thermal stability” mean kinetic inertness under 80 °C in this communication and dissociation occur to give radicals over 80 °C) (**Fig. 1c**). We expected that non-symmetric RMs that contain a cyanofluorene (CF) unit could be obtained via radical-exchange reactions from two parent RMs, and that such RMs would be relatively stable and hopefully isolable at room temperature if they incorporated a thermostable unit. Based on this hypothesis and with the thermostable RM DFSN in hand, we designed non-symmetric cyanofluorenyl/arylbenzofuranone (CF/ABF, **Fig. 1b**) derivatives whose central C–C bond is formed via a radical-exchange reaction between two different symmetric RMs, i.e., DFSN and DABBF. In response to mechanical stress, DFSN and the less thermally stable DABBF generate pink CF radicals and blue ABF radicals, respectively, through homolytic cleavage of their central C–C bonds. Therefore, the hybridization of these two mechanochromophores was expected to furnish a mechanochromophore with novel colour-change behaviour and multifunctionality derived from the simultaneous generation of

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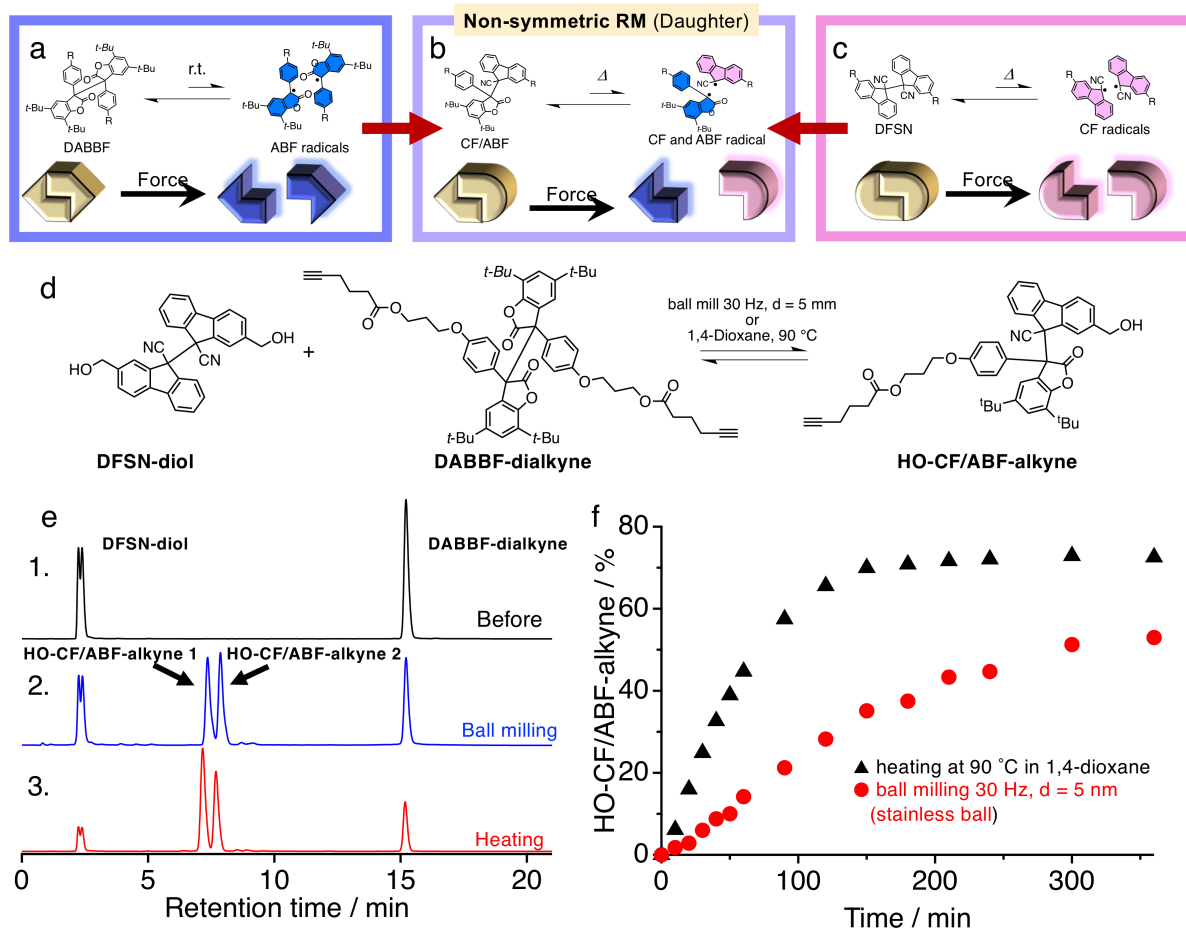


Fig. 1 Schematic illustration of non-symmetric RMs and equilibria of a) DABBF, b) CF/ABF and c) DFSN derivatives. d) Synthetic scheme of **HO-CF/ABF-alkyne**. e) HPLC profiles of before the exchange reaction (1), after exchange reaction by ball milling (2) and heating (3). Generation ratio of **HO-CF/ABF-alkyne** by radical exchange reaction by ball milling (red) and heating (black).

these two radicals in response to mechanical stress. The thermal stability and mechanoresponsiveness of the obtained CF/ABF derivatives were evaluated using electron paramagnetic resonance (EPR) measurements, which can quantify the amount of radicals generated. In addition, CF/ABF-centred polystyrene was synthesized, and its mechanochromic properties were investigated.

As shown in **Fig. 1d**, the non-symmetric RM **HO-CF/ABF-alkyne** was synthesized via the radical-exchange reaction between equimolar amounts of hydroxylated DFSN (**DFSN-diol**) and DABBF with two alkyne groups (**DABBF-dialkyne**) in 1,4-dioxane at 90 °C. Although DFSN produces few radical species at 90 °C (**Fig. S21**), the radical exchange reaction between DFSN and DABBF can be likely to proceed over 80 °C.²⁴ The radical exchange reaction between **DFSN-diol** and **DABBF-dialkyne** has also proceeded in the bulk state by ball milling, i.e., both thermal and mechanical stimuli can induce exchange reaction which was monitored using HPLC. In the heating system, the reaction reached equilibrium within ~3 h, resulting in separated HPLC peaks with a ratio **DFSN-diol** : **DABBF-dialkyne** : **HO-CF/ABF-alkyne** = 1:1:4.6 (**Figs 1e (3), S5**). In ball milling system, the reaction reached equilibrium within ~5 h, equilibrium ratio was 1:1:2 (**Fig. 1e (2), S6**). Density functional theory (DFT) calculations showed that DFSN is the most stable product

among these RMs, and CF/ABF is less stable than DFSN but more stable than DABBF by 3.0–4.0 kcal/mol (**Fig. S29**), but these are little difference. Therefore, the thermodynamic equilibrium ratio is expected to be statistical 1:1:2. In ball-milling reactions, the reactions reach thermodynamic equilibrium because the Gibbs free energy of the transition states (ΔG^\ddagger) is reduced by mechanical stimulation.²⁵ The equilibrium ratio of the bulk system (1:1:2) is expected to be originated from thermodynamic equilibrium of these RMs. On the other hand, the equilibrium ratio of the present heating system (1:1:4.6) might be originated from persistent radical effect.^{26, 27} Since the concentration of ABF radicals in this system is higher than that of CF radicals at 90 °C, selective recombination of CF and ABF radicals occurs, resulting in establishing a stationary state biased toward CF/ABF.

The exchange products, which comprise two diastereomeric compounds (**HO-CF/ABF-alkyne 1** and **HO-CF/ABF-alkyne 2**), were successfully isolated by column chromatography on silica gel and characterized by ¹H NMR, ¹³C NMR, and IR spectroscopy, as well as FAB mass spectrometry (**Fig. S1–S4**).

To evaluate the thermal stability of **HO-CF/ABF-alkyne**, variable-temperature EPR measurements of a solution of **HO-CF/ABF-alkyne 1** were carried out at 0–120 °C (**Fig. S19**). The generation of carbon-centred radical species by the homolytic

cleavage of its central C–C bonds was confirmed by the g value of 2.003. We calculated the dissociation ratio of CF/ABF at each temperature using 4-hydroxyl-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a standard. The dissociation ratio of CF/ABF was intermediate between those of DABBF and DFSN (e.g., CF/ABF: $3.5 \times 10^{-2}\%$; DABBF: $15 \times 10^{-2}\%$; DFSN: $0.015 \times 10^{-2}\%$ at 100°C) (Fig. 2).

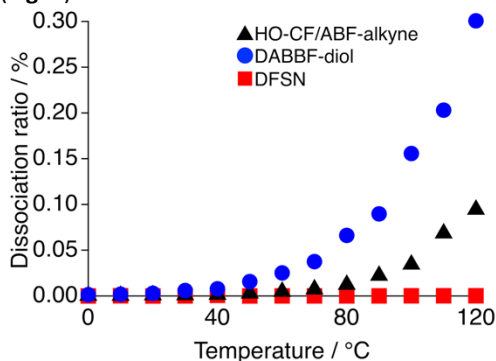


Fig. 2 Percentage of dissociated HO-CF/ABF-alkyne (black), DABBF-diol (blue), and DFSN (red) in anisole (25 mM) at various temperatures (0–120 °C).

The dissociation ratios indicate that the thermal stability of the mechanophores follows the order DFSN > CF/ABF > DABBF and that the CF unit endows the RM with thermal stability, which is almost four times higher than that of DABBF. The dissociation temperature of CF/ABF was estimated to be beyond 50°C , which suggests that CF/ABF exists in the coupled state at room temperature. To confirm the stability of CF/ABF, the free radical polymerization of methyl acrylate was attempted at room temperature in the presence of CF/ABF (Fig. S23). This reaction could not be achieved in the presence of DABBF, which acts as a radical polymerization inhibitor; the success of the reaction in the presence of CF/ABF indicates that radicals are not generated from CF/ABF at room temperature and demonstrates that hybridization is able to change the character of the RM.

CF/ABF was then incorporated into a polymer chain, as the responsiveness of mechanochromophores can be amplified upon incorporation into polymer chains. The hydroxy group on HO-CF/ABF-alkyne was converted into an alkyne group by reaction with 5-hexynoyl chloride to afford alkyne-CF/ABF-alkyne. In the presence of CuBr as a catalyst, the click reaction of alkyne-CF/ABF-alkyne and azide-terminated polystyrene ($M_n = 8.1$ kDa; PDI = 1.13) gave linear polystyrene with a CF/ABF unit at the centre of the polymer main chain as a white powder (PS-CF/ABF-PS; Fig. 3a). Polystyrene was selected as the matrix polymer on account of its relatively high glass-transition temperature (T_g), which prevents the recombination of the radical species generated upon cleavage of the mechanochromophore. PS-CF/ABF-PS was characterized using ^1H NMR spectroscopy and size-exclusion chromatography (SEC). The ^1H NMR spectrum of PS-CF/ABF-PS showed the signals characteristic of the CF/ABF skeleton, while the SEC profile showed a unimodal peak corresponding to a molecular weight approximately twice that of the precursor (azide-terminated polystyrene), indicating the successful synthesis of PS-CF/ABF-PS ($M_n = 17$ kDa; PDI = 1.09). Polystyrene with DFSN and DABBF

at the centre of the polymer main chain was also synthesized and used as control samples (PS-DABBF-PS and PS-DFSN-PS).

The mechanochromic properties of PS-CF/ABF-PS were evaluated via ball milling (30 Hz, 10 min). Mechanoresponsiveness evaluation using ball mills has been investigated for various RMs^{9,10,24} and the mechanoresponsiveness of each RM can be quantitatively evaluated and compared by using polymers that have the same molecular weight. It revealed that the white powder became purple after milling (Fig. 3c). This colour change is probably due to a mixture of pink PS-DFSN-PS (Fig. 3b) and blue PS-DABBF-PS (Fig. 3d) after grinding under the same conditions. Solid-state UV-vis measurements were carried out to confirm the origin of the colour change. The UV-vis spectra showed absorption peaks derived from both CF and ABF radicals at 510 and 546 nm, respectively, suggesting that the purple colour was due to the simultaneous generation of CF and ABF radicals in response to mechanical force (Fig. 3e). In contrast, a mixture of the polymers PS-DABBF-PS and PS-DFSN-PS (1:1, w/w) showed only blue colouration after grinding, and peaks derived from the CF radicals were not observed in the UV-vis spectrum. This is because the DFSN moiety in the polymer chain is less mechanoresponsive than the DABBF moiety and produces thus a smaller number of pink CF radicals relative to the number of the blue ABF radicals (Fig. S23–S26). Non-symmetric RMs are useful in that they can achieve colour changes that cannot be achieved with polymer blends.

Moreover, EPR measurements were carried out to confirm that the colour change was due to the generation of radical species (Fig. 3f). The EPR analysis confirmed the generation of carbon radicals ($g = 2.003$) (Fig. S26), and the dissociation ratio of the CF/ABF skeleton of PS-CF/ABF-PS after grinding was estimated to be 0.90%, which falls between that of PS-DABBF-PS (2.48%) and PS-DFSN-PS (0.05%) (Fig. 3g). These results indicate that the mechanoresponsiveness of the polymers, calculated from the ratio of radical generation, followed the order PS-DABBF-PS > PS-CF/ABF-PS > PS-DFSN-PS, whereby the newly formed C–C bond exhibits intermediate mechanoresponsiveness. In other words, the main defect of the thermally stable DFSN as an RM, i.e., its reduced mechanoresponsiveness, was overcome by hybridization with DABBF. These results are consistent with the binding stability trend of the solution systems, supporting the hybridization of the mechanophores and showing that hybridization can control the mechanoresponsiveness.

In summary, we have demonstrated the synthesis of the novel non-symmetric radical-type mechanophore CF/ABF through the covalent recombination of the radicals of the parent mechanophores, DABBF and DFSN. CF/ABF derivatives were successfully synthesized by two different methods, heating and ball milling. EPR and UV-vis measurements showed that the thermal stability of the mechanophores followed the order DFSN > CF/ABF > DABBF, and that their mechanoresponsiveness decreased in the order DABBF > CF/ABF > DFSN. As expected, the daughter mechanophore CF/ABF exhibits properties intermediate to those of its parents. The tuned thermal stability of CF/ABF made it possible to apply

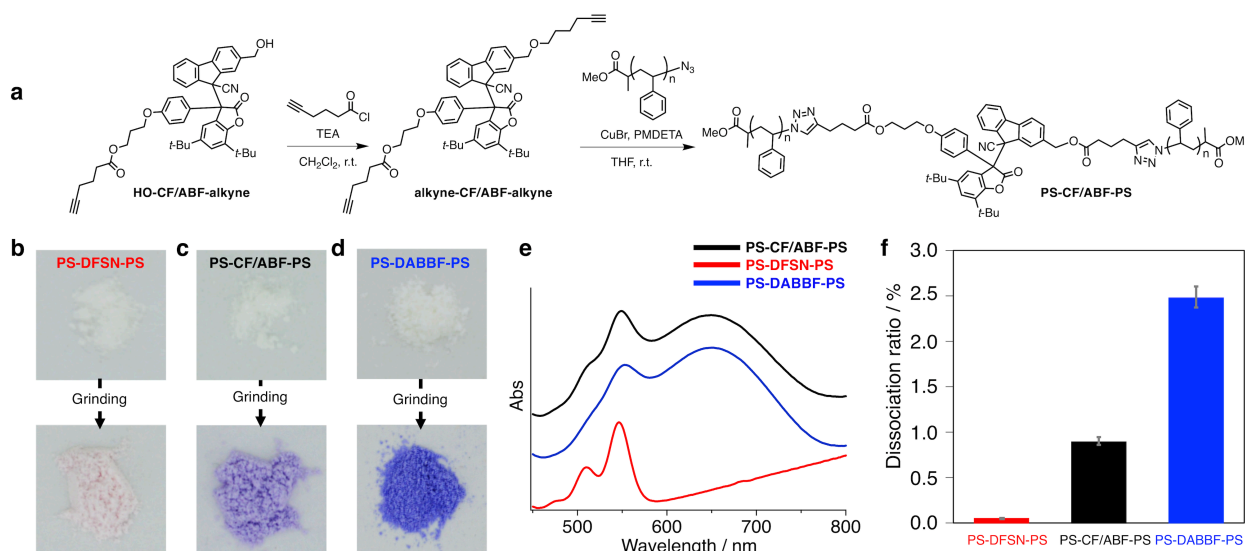


Fig. 3 a) Synthetic route to alkyne-CF/ABF-alkyne and PS-CF/ABF-PS. Photographs before and after grinding of b) PS-DFFSN-PS ($M_n = 16$ kDa), c) PS-CF/ABF-PS ($M_n = 17$ kDa), and d) PS-DABBF-PS ($M_n = 17$ kDa) at 25 °C in air. Solid-state UV-vis spectra of PS-CF/ABF-PS (black), PS-DABBF-PS (blue), and PS-DFFSN-PS (red) after grinding. f) Dissociation ratio (%) of PS-DFFSN-PS (red), PS-CF/ABF-PS (black), and PS-DABBF-PS (blue) after grinding.

ABF radicals to radical polymerization processes. Upon grinding, mixed colouration was observed due to the simultaneous generation of CF and ABF radicals, demonstrating the possibility of designing multifunctional polymers based on the simultaneous generation of heterogeneous radicals from non-symmetric mechanophores. We are currently investigating mechanical and mechanochromic properties of cross-linked polymers with CF/ABF units at the cross-linking points. Furthermore, the concept of non-symmetric RMs can be expected to provide access to a variety of functions and characteristics depending on the choice of parent RMs, and to open up new possibilities for RMs.

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Conflicts of interest

There are no conflicts to declare.

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