Development of a Thermally Stable Fluorescent Mechanophore and Its Application to Mechanochromic Polymers

(*Department of Chemical Science and Engineering, Institute of Science Tokyo*) ○Yuto Uchida, Hajime Sugita, Akira Takahashi, Hideyuki Otsuka

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Color-changing polymeric materials that respond to mechanical stimuli have great potential for various applications such as stress-sensing. A common approach for these materials is the incorporation of mechanophores into polymer chains. Radical-type mechanophores (RMs), which generate colored and/or fluorescent radical species via homolysis of a specific C–C bond, allow not only visualization of mechanical stress but also quantitative evaluation of the homolysis by electron paramagnetic resonance spectroscopy. However, most RMs also respond to thermal stimuli, limiting their range of applications. For example, tetraarylsuccinonitrile (TASN) is a valuable mechanophore as it mechanically generates fluorescent diarylacetonitrile (DAAN) radicals (**Fig. 1a**), but is also susceptible to temperature change.[1,2] In this study, we investigated diarylacetonitrile-α-carboxylic ester (DAANAC) derivatives as new RM units with high thermal stability.

A DAANAC-containing dimethacrylate cross-linker was synthesized and subjected to free-radical copolymerization with methyl acrylate (MA) to afford a DAANAC-cross-linked PMA (**CP$_{\mathbf{DAANAC}}$**) (**Fig. 1b**). Elongation of **CP$_{\mathbf{DAANAC}}$** showed yellow fluorescence under UV irradiation, demonstrating the generation of DAAN radical (**Fig. 1c, d**). These results suggest that the DAANAC skeleton can serve as a thermally stable RM, which can visualize mechanical stress by the generation of fluorescent DAAN radicals.

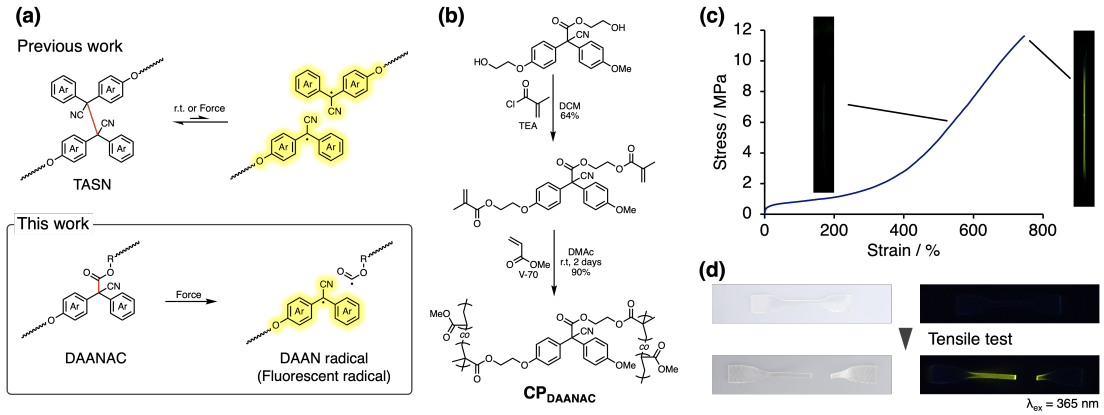

Fig. 1 (a) Conceptual illustration of this work. (b) Synthetic routes of **CP$_{\mathbf{DAANAC}}$**. (c) Representative stress–strain curve of **CP$_{\mathbf{DAANAC}}$** (10 mm/min). (d) Photographs of **CP$_{\mathbf{DAANAC}}$** under room light (left) and UV irradiation (right) before (top) and after tensile test (bottom).

1) H. Otsuka *et al.*, *Chem. Commun.* **2017**, *53*, 11885.
2) H. Otsuka *et al.*, *Nat. Commun.* **2021**, *12*, 126.