

論文 / 著書情報  
Article / Book Information

題目(和文)	安定なラジカル型メカノクロモフォア的设计に関する理論的および実験的研究
Title(English)	Theoretical and Experimental Studies on the Design of Stable Radical-type Mechanochromophores
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## Dissertation outline:

This dissertation has presented the attempts to synthesize a variety of radical-type mechanochromophores. By characterizing the stabilities as well as the degradation pathways of these radical-type mechanochromophores, a rational method to design organic radicals with desired stabilities was proposed, based on the correlation between experimental observations and theoretical quantum-chemical calculations. The method was further utilized to design a series of thermally stable radical-type mechanochromophores.

In Chapter 1, the background and objective of this dissertation were elaborated. Early research about mechanophores was reviewed, followed by a perspective on the current trend to design novel mechanochemical motifs. Then, a special class of mechanophore, namely mechanochromophore was introduced. Particularly, the charm of multi-color mechanochromism was appreciated for the potential application to differentiate both the type and the amplitude of applied mechanical stimulus. Radical-type mechanochromophores were then introduced as an interesting class of mechanochromophores, for that the mechanochemical reactions to generate stable radicals not only exhibit qualitative color change, but also allow quantitative analysis via electron paramagnetic resonance (EPR) analysis. Nevertheless, the poor thermal stabilities of common radical-type mechanochromophores have long been a limitation for further applications. As the examples of thermally stable radical-type mechanochromophores were quite limited, establishing a methodology to design such mechanochromophores remained challenging, which was the major issue solved in this dissertation.

In Chapter 2, bis[9-(4-methyl)phenyl-9-fluorenyl] peroxide (BMPF) was derived as the degradation product of phenylfluorenyl radical via aerobic peroxidation. The mechanochemical reaction of the BMPF motif was characterized and the mechanism was understood. It was revealed that the BMPF unit underwent a cleavage at peroxide linkage to give oxygen radicals, which were further degraded via a  $\beta$ -scission pathway to produce 9-fluorenone and phenyl radicals. The mechanochemical reaction mechanism was further utilized to fabricate a network polymer able to release fluorescent 9-fluorenone and exhibit mechanofluorescence upon mechanical stimuli such as grinding and compression. Moreover, the BMPF motif exhibited good reaction compatibility and satisfying thermal stability that could tolerate high temperatures up to 110 °C.

In Chapter 3, an RSE/SOMO combined *ab initio* approach to predict the stabilities and degradation pathways of organic radicals was proposed. 19  $\sigma$ -dimers of organic radicals from 3 major categories were synthesized and their stabilities with respect to the two

major degradation pathways of organic radicals, namely dimerization and peroxidation, were characterized. The experimental facts were further correlated with the computational results derived from quantum chemical calculations. The results revealed an approximately linear relationship between RSE values and the natural logarithms of dimer-radical dissociation constants, as well as a strong correlation between SOMO energies and the first-order rate constants of aerobic peroxidation.

In Chapter 4, the conclusion derived in Chapter 3 was applied to design radical-type mechanochromophores with high thermal stabilities. In detail, organic radicals with electron deficiencies were revealed to have strong tendencies to associate with their  $\sigma$ -dimers. Accordingly, the dicyano(4-methoxyphenyl)acetate (DCMPA-1) motif with an electron-deficient skeleton was designed and synthesized. Further characterizations about the reaction tolerance as well as the thermal stability of DCMPA-1 indicated that DCMPA-1 had a threshold temperature for dissociation at about 50 °C. Then, DCMPA derivatives with more meta methoxy groups, which were electron-withdrawing groups to endow the skeletons with more electron deficiency, were synthesized. These derivatives exhibited even better thermal stabilities than DCMPA-1. In addition, all the four DCMPA derivatives were integrated into polymer networks via free radical polymerization. The resulting polymers exhibited mechanochromism of red, green, and blue, which were the three primary colors of light.

The methodology to design stable radical-type mechanophores was successfully established in this dissertation. Applying the same strategy, it should be also possible to design organic radicals with designated reactivity or stability. The findings in this dissertation were expected to pave the way for the applications of functional materials that engage with organic radicals into practical cases.