

高分子鎖切断を検出可能な蛍光ラジカル前駆体の分子設計

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Molecular Design of Fluorescent Radical Precursors for Detecting Polymer Chain Scission
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Diarylacetonitrile (DAAN) derivatives are fluorescent molecular probes, which can detect mechanoradicals generated by polymer chain scission. DAAN reacts with highly reactive mechanoradicals to produce DAAN radicals. Since DAAN radicals are relatively stable radicals that emit fluorescence upon UV irradiation, it is possible to evaluate polymer main-chain scission in a complementary manner using fluorescence intensity and electron paramagnetic resonance (EPR) measurements. On the luminescence properties of open-shell radicals, however, since many radicals act as quenching groups, the number of reports of the luminescent radical is still limited and therefore their relationship between structure and fluorescence properties has not been fully investigated. In this study, we designed and synthesized a series of DAAN derivatives with different substituents and investigated their properties. As a result, the fluorescence wavelength and mechanoradical detectability can be systematically tuned by changing the substituents of DAAN derivatives.

Keywords : Fluorescent radical; Mechanochemistry; Mechanoradical; Molecular probe

ジアリールアセトニトル (DAAN) 誘導体は、高分子鎖切断によって発生するメカノラジカルと反応することで安定な DAAN ラジカルを生じ、紫外光照射下で蛍光発光を示す分子プローブである (Fig. 1a)¹⁾。しかし、蛍光性を示すラジカルの報告例は限られており、未だラジカルの構造と蛍光の関係性については明らかにされていない。本研究では、置換基の異なる DAAN 誘導体をポリスチレンとともにすり潰し、発生する DAAN ラジカルを電子スピン共鳴測定、蛍光スペクトル測定により評価した。その結果、置換基を変化させることで、ラジカル種の蛍光波長やメカノラジカル検出能を系統的に制御できることが示唆された (Fig. 1b)。

1) T. Yamamoto, S. Kato, D. Aoki, H. Otsuka, *Angew. Chemie. Int. Ed.*, **60**, 2680 (2021).

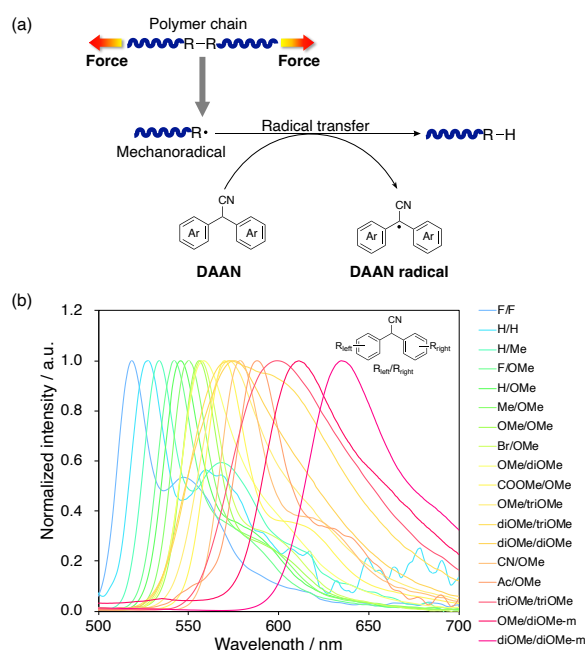


Fig. 1 (a) Radical transfer reactions of DAAN derivatives by polymeric mechanoradicals. (b) Normalized fluorescent spectra of DAAN radicals ($\lambda_{\text{em}} = 365 \text{ nm}$).