アニオン性ヘプタメチンシアニン色素の特性における置換基の効果

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Effect of Substituents on the Properties of Anionic Heptamethine Cyanine Dyes (¹Department of Materials Science and Processing Graduate School of Natural Science and Technology, Gifu University, ²Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, ³Life Science Research Center Division of Instrumental Analysis, Gifu University) OYuta Arisawa, ¹ Yasuhiro Kubota, ² Toshiyasu Inuzuka, ³ Kazumasa Funabiki²

As one of the organic dyes selectively absorbing near-infrared light, there are heptamethine cyanine dyes. Among them, many examples having a cationic skeleton have been reported. However, there are only few reports on the heptamethine cyanine dyes which have an anionic skeleton. We have developed a novel dye carrying fluorine-containing substituents in anionic heptamethine cyanine dye and evaluated its thermal- and photo-stabilities.

In this study, we newly synthesized dyes carrying the various substituents at the meso position of the cyclohexene ring. In previous studies, we found that the maximum absorption wavelength (λ_{max}) of $\mathbf{5a}$, in which perfluorophenyl groups were introduced into the known dye $\mathbf{5c}$, was red-shifted (18 nm)¹). It was found that the λ_{max} was further red-shifted (13 nm) in $\mathbf{6a}$ in which the sulfur atom was introduced at the meso position of the cyclohexene ring portion, which was newly synthesized this time.

Keywords: Organic Dyes; Near-Infrared Light; Fluorine Substituents; Cyanine Dyes

近赤外光を選択的に吸収できる有機色素の1つとして、ヘプタメチンシアニン色素がある。そのヘプタメチンシアニン色素の中で、母骨格がカチオン性のものに関しては多くの利用例や報告例がある。しかし、母骨格がアニオン性の色素に関しては少ない。我々はこれまでに、既知のアニオン性ヘプタメチンシアニン色素にフッ素置換基を導入した新規な色素を開発し、その耐熱性や耐光性を評価してきた。

本研究では、新たに色素骨格中心のシクロヘキセン環部分のメソ位に各種置換基を有する色素を合成し、その特性を評価した。これまでの研究で、既知の色素 5c にペルフルオロフェニル基を導入した 5a では、その最大吸収波長 (λ_{max}) が 18 nm 長波長化することを見いだした 1)。今回新たに合成したシクロヘキセン環部分のメソ位に S 原子を導入した 5c では、さらに λ_{max} が 13 nm 長波長化することがわかった。(Fig 2.)

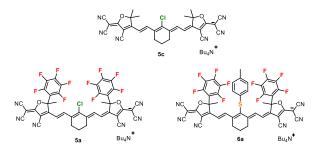


Fig 1. Structures of heptamethine cyanine dyes

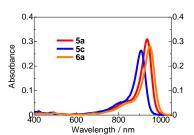


Fig 2. UV-Vis-NIR spectra of the dyes 5a, c, 6a in CH₂Cl₂ solution

1) 有澤, 船曳ら, 2020 年度色材研究発表会, P14; 有澤, 船曳ら, 第43 回フッ素化学討論会, P20.