NO.1

Year 2023	**Summary of Thesis**

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(Title)

Optical properties of methyl salicylate derivatives with an anchor site for self-assembling

A dyad-type molecule (MS-dyad) consisting of two methyl salicylate (MS) molecules linked by a sigma chain forms a stable aggregate under high concentration conditions (~10-2 M) and gives characteristic absorption and fluorescence spectra with a small Stokes shift and an oscillatory structure in the longer wavelength region than when the molecule is alone (M. Takahashi, et.al., *J. Phys. Chem. B*, 2022, **126**, 3116) In this study, mainly for the purpose of identifying the anchoring site necessary for MS to form stable aggregates, we synthesized (1) molecules in which one MS side was replaced with a benzene ring (MS-Bz) and (2) molecules in which an alkoxy chain (n = 2-10) was linked to MS (C2~C10), as shown in **Fig. 1,** and evaluated their accumulation properties.

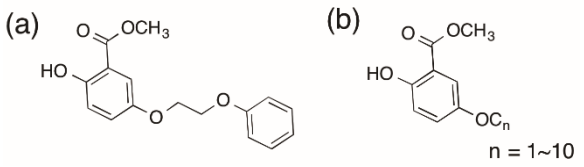

Fig.1 Chemical structural formulas of the methyl salicylate (MS) derivatives covered in this study. (a) MS-Bz, (b) alkoxylated MS (denoted C1~C10).

(1) MS-Bz: As in the case of MS-dyad, characteristic absorption and fluorescence spectra appeared with increasing dye concentration, indicating that stable aggregates can be obtained if MS is placed on one side of the molecule. On the other hand, compared to MS-dyad, an aggregate-derived absorption band with a maximum at 465 nm in CHCl3 solution began to appear at concentrations lower than 10-2 M, suggesting improved accumulation (**Fig. 2**).

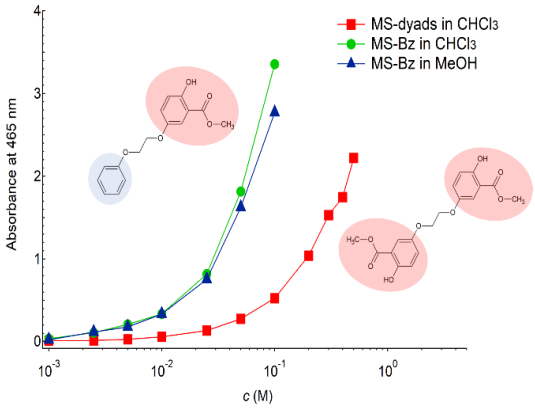

Fig.2 Absorbance change of the aggregate-derived absorption band with respect to dye concentration.

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NO . 2

(2) Alkoxylated MS: While the commercially available C1 is a clear liquid, the synthesized C2 and C3 were obtained as light yellow powder, C4~C7 as yellow liquid, and C8~C10 as yellow powder, and characteristic absorption and fluorescence spectra derived from aggregates were observed in the samples above C4. Thus, it is clear that linear hydrocarbon chains of C4 or higher can function as anchors for the formation of stable aggregates. Regardless of the carbon number, the powder sample dissolved at high temperatures and turned into a yellow liquid showing aggregate-derived green fluorescence. Differential scanning calorimetry (DSC) was therefore performed to investigate the correlation between chain length, melting temperature, and fluorescence properties.

In the powder sample, an endothermic peak due to melting was observed during the temperature increase, and an exothermic peak due to crystallization was observed during the temperature decrease, regardless of the carbon number (**Fig. 3**(a)). On the other hand, for liquid samples of C1, C4, C6, and C7, an endothermic peak due to melting was observed during the temperature increase process, but no exothermic peak due to crystallization was observed during the temperature decrease process. However, in the case of C6 and C7, an exothermic peak due to crystallization was observed during the temperature increase process in the low temperature range (below 0°C) (**Fig. 3**(b)). Such a change in the DSC curve indicates that the liquid state is maintained below the melting point without crystallization (undercooled state), and then crystallizes upon heating, which is called "cold crystallization. Recently, materials that exhibit cold crystallization are expected to be applied as heat storage materials (K. Turunen, et.al., *Appl. Energy*, 2020, **266**, 114890), but the target materials are mainly polymeric compounds. In addition, alkoxylated MS is promising as a new heat storage material, because the heat storage and heat dissipation processes can be distinguished by the fluorescent color change.

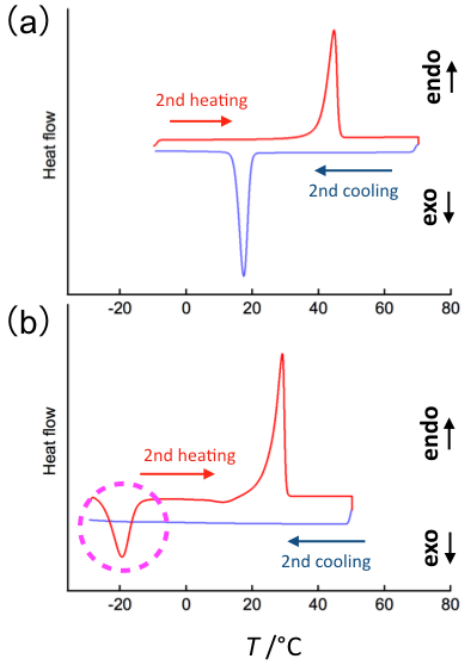

Fig.3 DSC measurements of (a) yellow powder C8, (b) yellow liquid C7. Scanning speed 10°C/min).

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