Synthesis of triarylsulfoniums containing electron-donating groups and their applications to cationic functional groups with excellent alkaline-resistant performance

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To realize the low-cost hydrogen production system, the water splitting module that operates under alkaline conditions is paid much attention since it does not require noble metals such as Pt for electrodes. However, due to the low chemical stability of the anion-exchange membrane (AEM) which consists of polymers possessing cationic functional groups, modules that exhibit sufficient durability have scarcely been realized yet.

We have been working on the development of alkaline-tolerant triarylsulfonium (**TAS**) structures that are potentially applicable to cationic functional groups in robust AEM materials. Based on the synthetic methods including the Friedel-Crafts reaction using diaryl sulfoxides, **TAS**s with excellent alkaline stability were developed by introducing sterically demanding substituents.[1)] For example, **TAS-cC** exhibits 25 times higher stability compared to benzyltrimethylammonium (BTMA), the commonly used cationic functional group for AEM materials. To develop further cations with much excellent alkaline-resistant properties, **TAS**s with electron-donating groups such as -NMe_2 and -OMe (**TAS-cC-NMe_2** and **TAS-cC-OMe**, respectively) were prepared by the post-functionalization of a fluorine-substituted reactive precursor (**Fig.1**). Especially, in the case of **TAS-cC-NMe_2**, it was surprising that no decomposition occurred even after 30 d in 2 M KOH/CD_3OH at 80 °C (**Fig. 2**). The synthesis of polymers containing alkaline-tolerant **TAS** units will also be described.

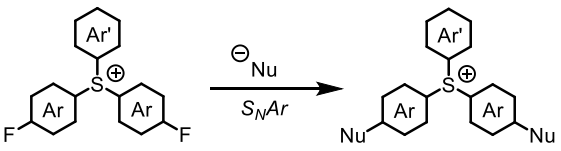

Fig. 1 Post-functionalization of **TAS**.

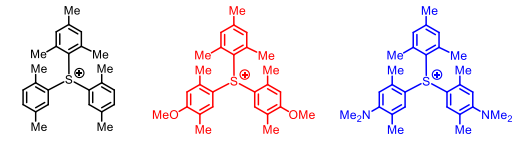

Fig. 2 Alkaline stability of functionalized **TAS** cations

1) T. Imai, R. Hifumi, S. Inagi, I. Tomita, *72nd SPSJ Symp. Macromol.*, **2023**, 2B18.