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# Liquid 2-Pyridinium Styryl Dyes having Oxaalkyl Units

Masaki MATSUI*,†, Yasuhiro KUBOTA* and Kazumasa FUNABIKI*

*Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu, Gifu 501-1193, Japan
† Corresponding Author, E-mail: matsuim@gifu-u.ac.jp

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**Abstract**

2-{4-[Bis(2,5-dioxa-7-heptanyl)amino]styryl}-1-(2,5,8-trioxa-10-octadecanyl)- and 1-(2,5,8-trioxa-10-octadecanyl)-2-{4-[bis(2,5,8-trioxa-10-octadecanyl)-amino]styryl}pyridinium bis(perfluorobutylsulfonyl)imide are liquid compounds at room temperature. The fluorescence intensity of these liquid derivatives in liquid nitrogen was enhanced *ca.* six-times compared with that at room temperature.

***Key-words***: *Pyridinium styryl dyes, Liquid dye, Fluorescence, Oxaalkyl group*

## 1. Introduction

Dyes and pigments, in which auxochromes such as amino, nitro, and hydroxyl groups are attached in a molecule, are usually solid. In principle, as organic dyes are aromatic compounds, they have strong π/π interactions in the solid state. Furthermore, these auxochromes can give strong polarity to the molecule and/or form hydrogen bonding to show high melting point. Recently, we have reported that any 7-substituted coumarins are liquid at room temperature[1]. Pyridinium cations and bis(perfluoroalkylsulfonyl)imide anions are important components of ionic liquids[2-4]. We consider that even polar cationic dyes in which these ionic liquid components are contained have potentials for liquid derivatives. In our previous paper, 2-[4-(didecylamino)styryl]-1-dodecylpyridinium bis(perfluorobutylsulfonyl)imide was reported to show very low melting point of 27.2 ˚C[5]. In the case of alkyl groups, Van der Walls interactions exist between them. Meanwhile, oxaalkyl groups have intermolecular repulsion between the oxygen atoms due to lone electron pairs on the oxygen atom(s). Therefore, oxaalkyl groups can show weaker intermolecular interactions than alkyl groups. In fact, the melting point, which reflects the degree of intermolecular interactions, of oxaalkyl derivatives is lower than that of the alkyl derivatives[6]. Though many kinds of cationic styryl dyes are known, no liquid derivatives have been reported so far. On the basis of these points, though practical applications of liquid dyes have not been found yet, we hereby report the preparation of liquid styryl dyes in this paper.

## 2. Experimental

### 2.1 Instruments

Melting points were measured with a Yanagimoto MP-S2 micro-melting-point apparatus and SII Technology Co., EXSTAR-6000 instrument. NMR spectra were obtained by a JMN α-400 spectrometer. IR spectra were taken by a Shimadzu Affinity-1 spectrophotometer. UV-vis absorption and fluorescence spectra were taken on Hitachi U-3500 and JASCO FP8600 spectrophotometers, respectively. Fluorescence quantum yields were measured by a Hamamatsu Photonics Quantaurus QY C11347-01.

### 2.2 Materials

2-Methylpyridine (**1**) was purchased from Nacalai tesque, Inc. Lithium bis(perfluorobutylsulfonyl)imide (**16**) were purchased from Wako Chemical Industries, Ltd. 4-[Bis(2-oxa-4-butanyl)amino]benzaldehyde (**8**), 4-[bis(2,5-dioxa-7-heptanyl)amino]benzaldehyde (**9**), and 4-[bis(2,5,8-trioxa-10-octadecanyl)amino]benzaldehyde (**10**) were prepared as described in the literature[6].

### 2.3 Synthesis of 1-oxaalkyl-2-methylpyridinium tosylates 5-7

To an acetonitrile solution (10 mL) of 2-methylpyridine (**1**) (0.93 g, 10 mmol) was added oxaalkyl tosylates **2**-**4** (12 mmol). The mixture was refluxed for 2 days. After the reaction was completed, the reaction mixture was poured into ether. The resulting precipitate was washed with ether and dried. The product was used without further purification. The physical and spectral data are shown below.

*2-Methyl-1-(2-oxa-4-butanyl)pyridinium tosylate (**5**)*

Yield 92 %; oil; $^1$H NMR ($CDCl_3$) $\delta$ = 2.33 (s, 3H), 2.87 (s, 3H), 3.23 (s, 3H), 3.85 (t, $J$ = 4.2 Hz, 2H), 4.97 (t, $J$ = 4.2 Hz, 2H), 7.12 (d, $J$ = 8.0 Hz, 2H), 7.71 (d, $J$ = 8.0 Hz, 2H), 7.72 (d, $J$ = 7.4 Hz, 1H), 7.85 (t, $J$ = 7.4 Hz, 1H), 8.23 (t, $J$ = 7.4 Hz, 1H), 9.21 (d, $J$ = 7.4 Hz, 1H); $^{13}$C NMR ($CDCl_3$) $\delta$ = 21.1, 21.2, 57.6, 59.0, 71.0, 125.86. 125.86 (2C), 128.6 (2C), 129.3, 139.2, 143.5, 144.7, 147.0, 155.7; IR (KBr) $\nu$ = 1521, 1478, 1457, 1208, 1192, 1121; Anal. Found: C, 59.51; H, 6.30; N,