

Original Research Paper

J. Jpn. Soc. Colour Mater., **87** [1], 3–12 (2014)

Low Melting-Point 2-Pyridinium Styryl Dyes

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: matsui@gifu-u.ac.jp

(Received July 21, 2013; Accepted December 25, 2013)

Abstract

The melting point of 1-alkyl-2-[4-(dialkylamino)styryl]pyridinium dyes was found to depend on the counter anions and the alkyl substituents. The counter anion had the greater influence, with the melting point ranging from 249 to 81.6°C in 1-butyl-2-[4-(diethylamino)styryl]pyridinium dyes. Then, the melting point was affected by the alkyl substituents. 2-[4-(Didecylamino)styryl]-1-dodecylpyridinium bis(perfluorobutylsulfonyl)imide exhibited the lowest melting point at 27.2°C.

Key-words: Styryl dyes, Low melting point, Alkyl group, Counter anion

1. Introduction

We sometimes realize that the physical properties of dyes such as solubility into organic solvents and melting point vary widely when changing the alkyl substituent(s) during the synthesis of a series of derivatives. Though the thermal behavior is usually examined in the field of liquid crystals, no systematic studies on the physical properties of dyes have been reported so far. Cationic styryl dyes are interesting compounds having potential applications for fluorescence probes¹⁻⁵), sensitizers^{6,7}), sensors⁸), two-photon absorption materials^{9,10}), non-linear optical materials^{11,12}), information recording materials¹³), and radical initiators¹⁴). As cationic styryl dyes cover the wide range of UV-vis absorption and fluorescence bands, it is of significance to examine their physical properties by changing the counter anion and the alkyl substituent(s). The effect of an alkyl group in pyridinium styryl dyes on the solvatochromism¹⁵) and the affinity for surfactants have been reported^{16,17}). When the melting point is low, the material is not easily solidified even at low temperature. From the viewpoint of practical use, low melting point and high solubility result in improved processability. Though cationic 2-pyridinium styryl dyes are readily soluble in polar solvents such as alcohols, acetone, and DMF, they are usually insoluble in non-polar hexane. The organic moiety in 2-pyridinium styryl dyes can show affinity for hexane depending on the structure. In our previous paper, liquid 7-substituted 4-methylcoumarins have been reported¹⁸). This motivated us to find low melting-point cationic dyes. We report herein the effect of counter anion and alkyl groups on the melting point of 2-pyridinium styryl dyes.

2. Experimental

2.1 Instruments

Melting points were measured with Yanagimoto MP-52 micro-melting-point apparatus and SII Technology Co., EXSTAR-6200 instrument. NMR spectra were obtained by a JEOL JMN α -400 spectrometer. IR spectra were taken on a Shimadzu Affinity-1 spectrophotometer. Elemental analysis was performed on Yanaco CHN corder MT-6. 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 Quantaaurus-QY.

2.2 Materials

2-Methylpyridine (**1**) was purchased from Nacalai Tesque, Inc. Methyl iodide (**2**), ethyl bromide (**3**), 1-bromobutane (**4**), 1-iodooctane (**5**), 1-iodododecane (**6**), 4-(diethylamino)benzaldehyde (**14**), lithium 4,4,5,5,6,6-hexafluorodihydro-4H-1,3,2-dithiazine 1,1,3,3-tetraoxide (**30**), and lithium bis(perfluorobutylsulfonyl)imide (**32**) were purchased from Wako Chemical Industries, Ltd. Octadecyl iodide (**7**), lithium trifluoromethanesulfonate (**29**), and lithium bis(trifluoromethylsulfonyl)imide (**31**) were purchased from Tokyo Chemical Industry Co., Ltd., Sigma-Aldrich Co., Ltd., and Kanto Chemical Co., Inc., respectively. 4-(Dibutylamino)benzaldehyde (**15**), 4-(dioctylamino)benzaldehyde (**16**), 4-(didecylamino)benzaldehyde (**17**), and 4-(didodecylamino)benzaldehyde (**18**) were prepared as described in the literature¹⁹).

2.3 Synthesis of 1-alkyl-2-methylpyridinium halides **8-13**

To 2-methylpyridine (**1**) (1.85 g, 20 mmol) (**8**, methanol (13 mL); **9**, ethanol (13 mL); **10**, 1-butanol (13 mL); **11-13**,