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Liquid 2-Pyridinium Styryl Dyes having Oxaalkyl Units

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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 temperature¹⁾. Pyridinium cations and bis(perfluoroalkylsulfonyl)imide anions are important components of ionic liquids²⁻⁴⁾. 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 °C⁵⁾. In the case of alkyl groups, Van der Waals 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 derivatives⁶⁾. 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 Quantaaurus 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 literature⁶⁾.

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; ¹H NMR (CDCl₃) δ = 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); ¹³C NMR (CDCl₃) δ = 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) ν = 1521, 1478, 1457, 1208, 1192, 1121; Anal. Found: C, 59.51; H, 6.30; N,

4.30 %. Calcd for $C_{16}H_{21}NO_4S$: C, 59.42; H, 6.54; N, 4.33 %.

1-(2,5-Dioxa-7-heptanyl)-2-methylpyridinium tosylate (6)

Yield 70 %; oil; 1H NMR ($CDCl_3$) δ = 2.33 (s, 3H), 2.89 (s, 3H), 3.24 (s, 3H), 3.37 (t, J = 4.5 Hz, 2H), 3.51 (t, J = 4.5 Hz, 2H), 3.99 (t, J = 4.5 Hz, 2H), 4.98 (t, J = 4.5 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 7.1 Hz, 1H), 7.83 (t, J = 7.1 Hz, 1H), 8.27 (t, J = 7.1 Hz, 1H), 9.28 (d, J = 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 21.0, 21.2, 57.6, 58.8, 69.7, 70.3, 71.4, 125.7, 125.8 (2C), 128.5 (2C), 129.4, 139.0, 143.9, 144.8, 145.0, 155.8; IR (KBr) ν = 1512, 1481, 1457, 1206, 1190, 1130; Anal. Found: C, 59.04; H, 6.78; N, 3.86 %. Calcd for $C_{18}H_{25}NO_5S$: C, 58.83; H, 6.86; N, 3.81 %.

2-Methyl-1-(2,5,8-trioxa-10-octadecanyl)pyridinium tosylate (7)

Yield 72 %; oil; 1H NMR ($CDCl_3$) δ = 2.32 (s, 3H), 2.87 (s, 3H), 3.33 (s, 3H), 3.46-3.52 (m, 8H), 3.94 (t, J = 4.8 Hz, 2H), 4.91 (t, J = 4.8 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 7.8 Hz, 2H), 7.79 (d, J = 7.3 Hz, 1H), 7.80 (t, J = 7.3 Hz, 1H), 8.28 (t, J = 7.3 Hz, 1H), 9.17 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 20.8, 21.1, 57.4, 58.8, 69.4, 70.0, 70.1, 70.2, 71.6, 125.5, 125.7 (2C), 128.4 (2C), 129.5, 138.8, 144.0, 144.9, 146.6, 155.7; IR (KBr) ν = 1517, 1473, 1457, 1206, 1191, 1128; Anal. Found: C, 58.12; H, 7.33; N, 3.60 %. Calcd for $C_{20}H_{29}NO_6S$: C, 58.37; H, 7.10; N, 3.40 %.

2.4 Synthesis of 1-oxaalkyl-2-[4-[bis(oxaalkyl)amino]-styryl]pyridinium tosylates 11-15

To an alcohol solution (20 mL, **11**, **12**: EtOH, **13**, **14**, **15**: BuOH) of 2-methyl-1-oxaalkylpyridinium tosylates **5-7** (8 mmol) was added 4-(oxaalkylamino)benzaldehyde **8-10** (5 mmol). The mixture was refluxed for 3 days. After the reaction was completed, the reaction mixture was concentrated. The product was purified by column chromatography (SiO_2 , $CHCl_3$ / MeOH = 10 / 1). The physical and spectral data are shown below.

1-(2-Oxa-4-butanyl)-2-[4-[bis(2-oxa-4-butanyl)amino]-styryl]pyridinium tosylate (11)

Yield 34 %; mp 143.5 °C; 1H NMR ($CDCl_3$) δ = 2.33 (s, 3H), 3.27 (s, 3H), 3.36 (s, 6H), 3.56 (t, J = 5.6 Hz, 4H), 3.63 (t, J = 5.6 Hz, 4H), 3.90 (t, J = 4.7 Hz, 2H), 5.02 (t, J = 4.7 Hz, 2H), 6.68 (d, J = 8.9 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 16.0 Hz, 1H), 7.49 (d, J = 16.0 Hz, 1H), 7.54 (t, J = 7.3 Hz, 1H), 7.56 (d, J = 8.9 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 8.11 (d, J = 7.3 Hz, 1H), 8.14 (t, J = 7.3 Hz, 1H), 8.91 (d, J = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 21.4, 50.9 (2C), 57.6, 59.1 (3C), 70.0 (2C), 70.6, 110.8, 111.8 (2C), 122.5, 123.1, 124.4, 126.0 (2C), 128.5 (2C), 131.1 (2C), 138.9, 143.1, 144.1, 144.7, 145.9, 150.4, 154.1; IR (KBr) ν = 1591, 1559, 1525, 1221, 1189, 1127; Anal. Found: C, 63.84; H, 7.22; N, 5.15 %. Calcd for $C_{29}H_{38}N_2O_6S$: C, 64.18; H, 7.06; N, 5.16 %.

1-(2,5-Dioxa-7-heptanyl)-2-[4-[bis(2-oxa-4-butanyl)amino]-styryl]pyridinium (12)

Yield 21 %; mp 56.6 °C; 1H NMR ($CDCl_3$) δ = 2.33 (s, 3H), 3.26 (s, 3H), 3.36 (s, 6H), 3.43 (t, J = 4.6 Hz, 2H), 3.55-3.69 (m, 6H), 3.64 (t, J = 5.7 Hz, 4H), 4.09 (t, J = 4.6 Hz, 2H), 5.09 (t, J = 4.6 Hz, 2H), 6.71 (d, J = 8.7 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 16.1 Hz, 1H), 7.45 (d, J = 16.1 Hz, 1H), 7.56 (t, J = 7.7 Hz, 1H), 7.57 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 8.0 Hz, 2H), 8.04 (d, J = 7.7 Hz, 1H), 8.13 (t, J = 7.7 Hz, 1H), 9.16 (d, J = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 21.1, 50.7 (2C), 57.3, 58.7, 58.9 (2C), 69.0, 69.8 (2C), 70.2, 71.4, 110.7, 111.6 (2C), 122.4, 122.9, 124.4, 125.8 (2C), 128.4 (2C), 130.8 (2C), 139.0, 143.2, 143.5, 144.5, 145.5, 150.2, 153.8; IR (KBr) ν = 1592, 1559, 1524, 1207, 1188, 1123; Anal. Found: C, 63.74; H, 6.82; N, 4.55 %. Calcd for $C_{31}H_{42}N_2O_7S$: C, 63.46; H, 7.22; N, 4.77 %.

2-[4-[Bis(2-oxa-4-butanyl)amino]styryl]-1-(2,5,8-trioxa-10-octadecanyl)pyridinium (13)

Yield 20 %; mp 16.4 °C; 1H NMR ($CDCl_3$) δ = 2.33 (s, 3H), 3.33 (s, 3H), 3.36 (s, 6H), 3.43 (t, J = 4.6 Hz, 2H), 3.52-3.58 (m, 8H), 3.63-3.65 (m, 6H), 4.08 (t, J = 4.6 Hz, 2H), 5.10 (t, J = 4.6 Hz, 2H), 6.71 (d, J = 9.4 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 16.7 Hz, 1H), 7.44 (d, J = 16.7 Hz, 1H), 7.58 (t, J = 7.9 Hz, 1H), 7.59 (d, J = 9.4 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 8.03 (d, J = 7.9 Hz, 1H), 8.12 (t, J = 7.9 Hz, 1H), 9.15 (d, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 21.1, 50.7 (2C), 57.2, 58.7, 58.8 (2C), 68.9, 69.8 (2C), 70.0, 70.1, 70.2, 71.5, 110.5, 111.6 (2C), 122.3, 122.9, 124.3, 125.8 (2C), 128.4 (2C), 130.8 (2C), 138.9, 143.2, 143.8, 144.5, 145.6, 150.2, 153.7; IR (KBr) ν = 1591, 1560, 1523, 1205, 1189, 1121; Anal. Found: C, 62.80; H, 7.16; N, 4.11 %. Calcd for $C_{33}H_{46}N_2O_8S$: C, 62.83; H, 7.35; N, 4.44 %.

2-[4-[Bis(2,5-dioxa-7-heptanyl)amino]styryl]-1-(2,5,8-trioxa-10-octadecanyl)pyridinium tosylate (14)

Yield 9 %; mp 16.7 °C; 1H NMR ($CDCl_3$) δ = 2.34 (s, 3H), 3.32 (s, 3H), 3.38 (s, 6H), 3.44-3.66 (m, 24H), 4.05 (t, J = 4.7 Hz, 2H), 5.06 (t, J = 4.7 Hz, 2H), 6.71 (d, J = 8.9 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 15.6 Hz, 1H), 7.43 (d, J = 15.6 Hz, 1H), 7.54 (t, J = 6.7 Hz, 2H), 7.63 (d, J = 8.9 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 6.7 Hz, 1H), 8.13 (t, J = 6.7 Hz, 1H), 9.02 (d, J = 6.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ = 21.0, 50.7 (2C), 57.1, 58.6, 58.8 (2C), 68.0 (2C), 68.7, 69.9 (2C), 70.0, 70.2, 70.3, 71.5, 71.6 (2C), 110.4, 111.4 (2C), 122.3, 122.9, 124.3, 125.8 (2C), 128.3 (2C), 130.8 (2C), 138.7, 143.2, 143.9, 144.5, 145.3, 150.0, 153.5; IR (KBr) ν = 1591, 1560, 1522, 1225, 1191, 1121; Anal. Found: C, 61.45; H, 7.32; N, 3.55 %. Calcd for $C_{37}H_{54}N_2O_{10}S$: C, 61.82; H, 7.57; N, 3.90 %.

1-(2,5,8-Trioxa-10-octadecanyl)-2-[4-[bis(2,5,8-trioxa-10-octadecanyl)amino]styryl]pyridinium tosylate (15)

Yield 10 %; mp 25.3 °C; ¹H NMR (CDCl₃) δ = 2.32 (s, 3H), 3.32 (s, 3H), 3.38 (s, 6H), 3.44-3.75 (m, 32H), 4.07 (t, *J* = 5.2 Hz, 2H), 5.07 (t, *J* = 5.2 Hz, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 15.8 Hz, 1H), 7.46 (d, *J* = 15.8 Hz, 1H), 7.54 (t, *J* = 6.9 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 6.9 Hz, 1H), 8.14 (t, *J* = 6.9 Hz, 1H), 9.05 (d, *J* = 6.9 Hz, 1H); ¹³C NMR (CDCl₃) δ = 20.9, 50.4 (2C), 56.9, 58.46, 58.54 (2C), 67.9 (2C), 68.0 (2C), 68.6, 69.75 (2C), 69.85 (2C), 70.0, 70.1, 70.2, 71.3, 71.4 (2C), 110.1, 111.3 (2C), 122.1, 122.7, 124.1, 125.6 (2C), 128.1 (2C), 130.6 (2C), 138.6, 143.1, 143.6, 144.4, 145.1, 149.9, 153.4; IR (KBr) ν = 1592, 1560, 1523, 1224, 1190, 1121; Anal. Found: C, 61.38; H, 7.42; N, 3.25 %. Calcd for C₄₁H₆₂N₂O₁₂S: C, 61.02; H, 7.74; N, 3.47 %.

2.5 Synthesis of 1-oxaalkyl-2-[4-[bis(oxaalkyl)amino]-styryl]pyridinium bis(perfluorobutylsulfonyl)imides 17-21

To a chloroform-methanol (1/1) mixed solution (5 mL) of 1-oxaalkyl-2-[4-(dioxyaalkylamino)styryl]pyridinium tosylates **11-15** (0.5 mmol) was added lithium bis(perfluorobutylsulfonyl)imide (16, 1.0 mmol) at ambient temperature. The mixture was stirred for 1 day. After the reaction was completed, the mixture was concentrated. The product was purified by column chromatography (Al₂O₃, CHCl₃ / MeOH = 100 / 1).

1-(2-oxa-4-butanyl)-2-[4-[bis(2-oxa-4-butanyl)amino]styryl]pyridinium bis(perfluorobutylsulfonyl)imide (17)

Yield 54 %; ¹H NMR (CDCl₃) δ = 3.30 (s, 3H), 3.35 (s, 6H), 3.57 (t, *J* = 5.4 Hz, 4H), 3.64 (t, *J* = 5.4 Hz, 4H), 3.84 (t, *J* = 4.6 Hz, 2H), 4.72 (t, *J* = 4.6 Hz, 2H), 6.73 (d, *J* = 9.2 Hz, 2H), 7.10 (d, *J* = 15.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.53 (d, *J* = 9.2 Hz, 2H), 7.56 (d, *J* = 15.8 Hz, 1H), 8.13 (d, *J* = 7.2 Hz, 1H), 8.18 (t, *J* = 7.2 Hz, 1H), 8.37 (d, *J* = 7.2 Hz, 1H); ¹⁹F NMR (CDCl₃, ext. CFCl₃) δ = -125.8 (4F), -120.9 (4F), -112.7 (4F), -80.7 (6F); IR (KBr) ν = 1597, 1567, 1531, 1352, 1239, 1195, 1171; Anal. Found: C, 37.70; H, 3.67; N, 4.41 %. Calcd for C₃₀H₃₁F₁₈N₃O₇S₂: C, 37.86; H, 3.28; N, 4.42 %.

1-(2,5-Dioxa-7-heptanyl)-2-[4-[bis(2-oxa-4-butanyl)amino]styryl]pyridinium bis(perfluorobutylsulfonyl)imide (18)

Yield 52 %; ¹H NMR (CDCl₃) δ = 3.26 (s, 3H), 3.36 (s, 6H), 3.42 (t, *J* = 4.4 Hz, 2H), 3.53-3.56 (m, 6H), 3.65 (t, *J* = 5.5 Hz, 4H), 3.99 (t, *J* = 4.4 Hz, 2H), 4.74 (t, *J* = 4.4 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 15.8 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 15.8 Hz, 1H), 8.13 (d, *J* = 7.7 Hz, 1H), 8.19 (t, *J* = 7.7 Hz, 1H), 8.43 (d, *J* = 7.7 Hz, 1H); ¹⁹F NMR (CDCl₃, ext. CFCl₃) δ = -125.9 (4F), -121.0 (4F), -112.8 (4F), -80.8 (6F); IR (KBr) ν = 1592, 1560, 1526, 1355, 1236, 1190, 1139; Anal. Found: C, 38.38;

H, 3.63; N, 4.19 %. Calcd for C₃₂H₃₅F₁₈N₃O₈S₂: C, 38.60; H, 3.54; N, 4.22 %.

2-[4-[Bis(2-oxa-4-butanyl)amino]styryl]-1-(2,5,8-trioxa-10-octadecanyl)pyridinium bis(perfluorobutylsulfonyl)imide (19)

Yield 58 %; ¹H NMR (CDCl₃) δ = 3.34 (s, 3H), 3.36 (s, 6H), 3.49 (t, *J* = 4.6 Hz, 2H), 3.53-3.59 (m, 8H), 3.63-3.67 (m, 6H), 4.00 (t, *J* = 4.6 Hz, 2H), 4.80 (t, *J* = 4.6 Hz, 2H), 6.75 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 15.4 Hz, 1H), 7.50 (t, *J* = 6.9 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 15.4 Hz, 1H), 8.06 (d, *J* = 6.9 Hz, 1H), 8.15 (t, *J* = 6.9 Hz, 1H), 8.57 (d, *J* = 6.9 Hz, 1H); ¹⁹F NMR (CDCl₃, ext. CFCl₃) δ = -125.9 (4F), -121.0 (4F), -112.8 (4F), -80.8 (6F); IR (KBr) ν = 1592, 1561, 1526, 1355, 1238, 1189, 1138; Anal. Found: C, 39.31; H, 3.78; N, 4.10 %. Calcd for C₃₄H₃₉F₁₈N₃O₉S₂: C, 39.27; H, 3.78; N, 4.04 %.

2-[4-[Bis(2,5-dioxa-7-heptanyl)amino]styryl]-1-(2,5,8-trioxa-10-octadecanyl)pyridinium bis(perfluorobutylsulfonyl)imide (20)

Yield 43 %; ¹H NMR (CDCl₃) δ = 3.33 (s, 3H), 3.38 (s, 6H), 3.46-3.67 (m, 24H), 3.99 (t, *J* = 4.4 Hz, 2H), 4.76 (t, *J* = 4.4 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 15.8 Hz, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 15.8 Hz, 1H), 8.10 (d, *J* = 7.3 Hz, 1H), 8.18 (t, *J* = 7.3 Hz, 1H), 8.52 (d, *J* = 7.3 Hz, 1H); ¹⁹F NMR (CDCl₃, ext. CFCl₃) δ = -125.9 (4F), -121.0 (4F), -112.8 (4F), -80.7 (6F); IR (KBr) ν = 1592, 1561, 1526, 1355, 1237, 1190, 1138; Anal. Found: C, 40.60; H, 4.26; N, 3.69 %. Calcd for C₃₈H₄₇F₁₈N₃O₁₁S₂: C, 40.47; H, 4.20; N, 3.73 %.

1-(2,5,8-Trioxa-10-octadecanyl)-2-[4-[bis(2,5,8-trioxa-10-octadecanyl)amino]styryl]pyridinium bis(perfluorobutylsulfonyl)imide (21)

Yield 53 %; ¹H NMR (CDCl₃) δ = 3.33 (s, 3H), 3.37 (s, 6H), 3.47-3.74 (m, 32H), 3.99 (t, *J* = 4.5 Hz, 2H), 4.76 (t, *J* = 4.5 Hz, 2H), 6.73 (d, *J* = 9.2 Hz, 2H), 7.12 (d, *J* = 16.3 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 9.2 Hz, 2H), 7.54 (d, *J* = 16.3 Hz, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 8.18 (t, *J* = 7.9 Hz, 1H), 8.51 (d, *J* = 7.9 Hz, 1H); ¹⁹F NMR (CDCl₃, ext. CFCl₃) δ = -125.8 (4F), -121.0 (4F), -112.8 (4F), -80.7 (6F); IR (KBr) ν = 1592, 1560, 1526, 1355, 1238, 1190, 1138; Anal. Found: C, 41.27; H, 4.50; N, 3.43 %. Calcd for C₄₂H₅₅F₁₈N₃O₁₃S₂: C, 41.48; H, 4.56; N, 3.46 %.

3. Results and Discussion**3.1 Synthesis**

Scheme 1 shows the synthesis of pyridinium styryl dyes **11-15** and **17-21**. 2-Methylpyridine (**1**) was *N*-alkylated with oxaalkyl tosylates **2-4** to give *N*-(oxaalkyl)pyridinium tosylates **5-7**, which were allowed to react with 4-[bis(oxaalkyl)amino]-benzaldehydes **8-10** to afford **11-15**. These compounds were

treated with lithium bis(perfluorobutylsulfonyl)imide (**16**) to provide **17-21**.

Solid derivatives were recrystallized from hexane. Liquid products were purified by column chromatography. When liquid products **20** and **21** were chilled by liquid nitrogen, they solidified. Then, after allowing them to stand at room temperature, they melted.

Fig. 1a depicts the effects of oxaalkyl group on the pyridinium-nitrogen on the differential scanning calorimetry (DSC) of bis(perfluorobutylsulfonyl)imide derivatives **17**, **18**, and **19**. The characteristic endothermic peaks corresponding to the melting point were observed at 72.8, 43.3, and 28.8 °C for **17**, **18**, and **19**, respectively. In the case of **18**, the glass transition temperature (T_g) was observed at around -23 °C. Thus, the longer the oxaalkyl unit on the pyridinium-nitrogen, the lower the melting point. The (2,5,8-trioxa-10-oxadecanyl) derivative **19** showed the lowest melting point.

The effects of oxaalkyl groups in 4-(bisoxaalkylamino)-phenylene moiety on the DSC of 2-[1-(2,5,8-trioxa-10-oxadecanyl)-pyridinium] bis(perfluorobutylsulfonyl)imide dyes **19**, **20**, and **21** are shown in **Fig. 1b**). Compounds **20** and **21** were chilled by liquid nitrogen before DSC measurements. Compound **20** showed small endothermic peak at around -50 °C followed by large one at -5.7 °C. A small peak coming

from contaminated water during the measurement is observed at 0 °C. Compound **21** indicated similar thermal behavior. A small endothermic peak at around -39 °C and large one at around -4.0 °C. The melting points of **20** and **21** are estimated to be -5.7 and -4.0 °C, respectively.

3.2 UV-vis absorption and fluorescence spectra

The UV-vis absorption and fluorescence spectra of **17-21** in dichloromethane are shown in **Fig. 2a**). The results are also listed in **Table 1**. They showed the absorption maximum ($\lambda_{\max}$) at around 495 nm with molar absorption coefficient (ϵ) of ca. 37,000. The fluorescence maxima ($F_{\max}$) were observed at around 590 nm with fluorescence quantum yield (Φ_f) of 0.09. Thus, no marked differences in the UV-vis absorption and fluorescence spectra were observed in dichloromethane. The fluorescence spectra of **17-21** in the crystalline or neat form are shown in **Fig. 2b**). The results are also listed in **Table 1**. The $F_{\max}$ was observed at around 650 nm, being bathochromic compared to those in dichloromethane, due to intermolecular interactions in the crystalline or neat form. The Φ_f of **17-21** in the crystalline or neat form was lower than that in dichloromethane. Compound **17** showed the highest Φ_f among, **17-21**, probably due to the highest melting point^{7,8}). Nevertheless, the liquid derivatives **20** and **21** exhibited red emission at around 650 nm in neat form with Φ_f of 0.02.

Fig. 1 DSC of **17-21**. Heated at 10 °C min⁻¹.

Fig. 2 UV-vis absorption and fluorescence spectra of **17-21**. a) measured in dichloromethane at the concentration of 1.0×10^{-5} mol dm⁻³ and b) measured in crystalline or neat form at room temperature.

Scheme 1 Reagents and conditions: i) **1** (1.0 equiv.), **2-4** (1.2 equiv.), MeCN, reflux, 2 d, ii) **5-7** (1.0 equiv.), **8-10** (1.0 equiv.), piperidine (a few drops), alcohol, reflux, 3 d, iii) **11-15** (1.0 equiv.), **16** (2.0 equiv.), rt, 1 d.

Table 1 Physical properties of 17-21.

Compd	m, n	mp/°C	In dichloromethane ^a			In crystalline or neat form		
			$\lambda_{\max}(\epsilon)/\text{nm}$	$F_{\max}/\text{nm}$	Φ_f	$\lambda_{\text{ex}}/\text{nm}$	$F_{\max}/\text{nm}$	Φ_f
17	1,1	72.8	496 (40,700)	591	0.10	522	653	0.08
18	2,1	43.3	496 (36,000)	590	0.09	584	653	0.02
19	3,1	28.8	494 (37,900)	589	0.09	587	661	0.02
20	3,2	-5.7	493 (35,900)	588	0.09	580 ^b	644 ^b	0.02 ^b
21	3,3	-4.0	494 (38,500)	590	0.09	582 ^b	651 ^b	0.02 ^b

^ameasured at the concentration of 1.0×10^{-5} mol dm⁻³.^bliquid. Fig. 3 Fluorescence spectra of 20 and 21. a) 20 ($\lambda_{\text{ex}} = 370$ nm) and b) 21 ($\lambda_{\text{ex}} = 370$ nm).

The fluorescence spectra of liquid derivatives 20 and 21 at room temperature and in liquid nitrogen is shown in Fig. 3. The fluorescence intensity of 20 and 21 in liquid nitrogen drastically increased (*ca.* 6-times) compared with that at room temperature. This result could come from the inhibition of free rotation of the oxaalkyl groups in the liquid styryl dyes at low temperature.

This is the first report not only of the preparation of liquid cationic styryl dyes but also that these liquid derivatives exhibit fluorescence in neat form.

4. Conclusion

Liquid styryl dyes, 2-{4-[bis(2,5-dioxa-7-heptanyl)amino]styryl}-1-(2,5,8-trioxa-10-octadecanyl)pyridinium and 1-(2,5,8-trioxa-10-octadecanyl)-2-{4-[bis(2,5,8-trioxa-10-octadecanyl)amino]styryl}pyridinium bis(perfluorobutylsulfonyl)-imides were obtained. Their fluorescence in neat form was enhanced *ca.* 6-times in liquid nitrogen.

References

- 1) S.-Y. Park, Y. Kubota, K. Funabiki, M. Matsui: *Chem. Lett.*, **38**, 162 (2009).
- 2) T. Welton: *Chem. Rev.*, **99**, 2071 (1999).
- 3) N. V. Piechikova, K. R. Seddon: *Chem. Soc. Rev.*, **37**, 123 (2008).
- 4) Y. Kohna, H. Ohno: *Chem. Commun.*, **48**, 7119 (2012).
- 5) M. Matsui, Y. Kubota, K. Funabiki: *J. Jpn. Soc. Colour Mater.*, **87**, 3 (2014).
- 6) M. Matsui, K. Noguchi, Y. Kubota, K. Funabiki: *Tetrahedron*, **66**, 9396 (2010).
- 7) M. Matsui, K. Ooiwa, A. Okada, Y. Kubota, K. Funabiki, H. Sato: *Dyes Pigm.*, **99**, 916 (2013).
- 8) P. An, Z.-F. Shi, W. Dou, X.-P. Cao, K.-L. Zhang: *Org. Lett.*, **12**, 4364 (2010).

オキサアルキルユニットを有する液体2-ピリジニウムスチリル色素

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要 旨

1-[4-ビス(2,5-ジオキサ-7-ヘプタニル)アミノ]スチリル-1-(2,5,8-トリオキサ-10-オクタデカニル) および 1-(2,5,8-トリオキサ-10-オクタデカニル)-2-[4-ビス(2,5,8-トリオキサ-10-オクタデカニル)アミノ]スチリルピリジニウムビス(ペルフルオロブチルスルホニル)イミドは室温で液体であった。これら液体誘導体の蛍光強度は、室温下と比較して約6倍であった。

キーワード：ピリジニウム＝スチリル色素, 液体色素, 蛍光, オキサアルキル基