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Solid-state fluorescence of pyridinium styryl dyes

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ABSTRACT

1-Alkyl-2-[4-(diethylamino)styryl]pyridinium salts showed fluorescence maxima at around 650 nm in the solid state depending on the alkyl group and counter anion. 1-Butyl-2-[4-(diethylamino)styryl]pyridinium bis(perfluorobutylsulfonyl)imide exhibited the fluorescence maximum at 652 nm with the highest quantum yield 0.16 in the crystalline form. The single X-ray crystallography suggests that this compound exhibits isolated dimer-type packing leading to fluorescence in the solid state.

1. Introduction

Cationic styryl dyes are interesting compounds having potential applications for fluorescence probes [1–5], sensitizers [6,7], sensors [8], two-photon absorption materials [9], nonlinear optical materials [10,11], information recording materials [12], and radical initiators [13]. The effect of an alkyl group in pyridinium styryl dyes on the solvatochromism [14] and the affinity for surfactants have been reported [15,16]. Though many papers concerning solid-state fluorescence have been reported, there is one paper describing the solid-state fluorescence of cationic compounds [17]. In the case of neutral fluorescent compounds, there are few compounds showing F_{max} beyond 700 nm. Cationic styryl dyes are easily prepared and can exhibit a wide range F_{max} by changing the electron-withdrawing ability of cationic heteroaromatic ring and electron-donating force of another aromatic moiety. Thus cationic styryl dyes have potential applications as solid-state fluorescent materials. We report herein the solid-state fluorescence of 1-alkyl-2-[4-(diethylamino)styryl]pyridinium dyes.

2. Results and discussion

2.1. Synthesis

Scheme 1 shows the synthesis of pyridinium styryl dyes **15**–**20** and **25**–**33**. 2-Methylpyridine (**1**) was *N*-alkylated with alkyl halides **2**–**7** to give 1-alkyl-2-methylpyridinium halides **8**–**13**, which were condensed with 4-(diethylamino)benzaldehyde (**14**) in the presence of piperidine to afford **15**–**20**. Then, these compounds were treated with lithium salts **21**–**24** to provide dyes **25**–**33**.

2.2. UV–vis absorption and fluorescence spectra

The UV–vis absorption and fluorescence spectra of **17** and **25**–**33** in dichloromethane are shown in Fig. 1. The absorption maximum (λ_{max}) was observed at around 510 nm with a molar absorption coefficient (ε) in the range of 39,400 to 45,500 mol^{-1} dm^3 cm^{-1}. The fluorescence maximum (F_{max}) was observed at around 594 nm with fluorescence quantum yields (Φ_f) in the range 0.10–0.12. Thus, no significant differences in the UV–vis absorption and fluorescence spectra were observed in solution.

The fluorescence spectra of **17** and **25**–**33** in the crystalline form are depicted in Fig. 2. Compounds **17** and **29** were recrystallized from toluene. Compounds **26** and **32** were from hexane–ethyl acetate mixed solvent. The other compounds were recrystallized from

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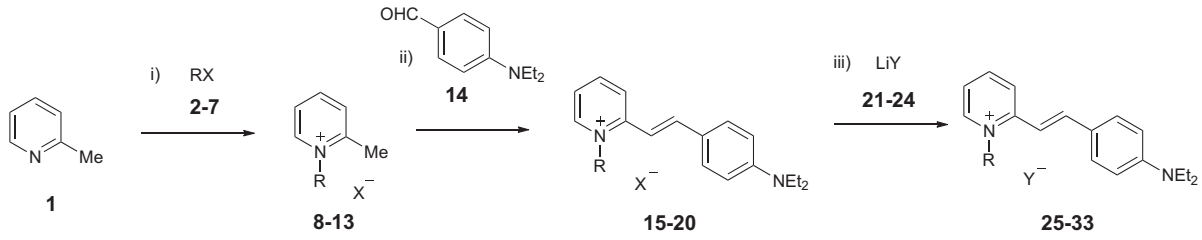

Compd	R	X
2, 8	Me	I
3, 9	Et	Br
4, 10	Bu	Br
5, 11	Oct	I
6, 12	Dodec	I
7, 13	Octadec	I

Compd	R	X
15	Me	I
16	Et	Br
17	Bu	Br
18	Oct	I
19	Dodec	I
20	Octadec	I

Compd	Y
21	CF_3SO_3
22	$(CF_2)_3(SO_2)_2N$
23	$(CF_3SO_2)_2N$
24	$(C_4F_9SO_2)_2N$

Compd	R	Y
25	Me	$(C_4F_9SO_2)_2N$
26	Et	$(C_4F_9SO_2)_2N$
27	Bu	CF_3SO_3
28	Bu	$(CF_3SO_2)_2N$
29	Bu	$(CF_2)_3(SO_2)_2N$
30	Bu	$(C_4F_9SO_2)_2N$
31	Oct	$(C_4F_9SO_2)_2N$
32	Dodec	$(C_4F_9SO_2)_2N$
33	Octadec	$(C_4F_9SO_2)_2N$

Scheme 1. Reagents and conditions: (i) **1** (1.0 eq), **2**–**7** (1.1 eq), alcohols, reflux, 5 d, (ii) **8**–**13** (1.0 eq), **14** (1.0 eq), piperidine, EtOH, reflux, 3 d, (iii) **15**–**20** (1.0 eq), **21**–**24** (1.25 eq), water/acetone = 2/1, r.t., 1 d.

hexane. The F_{max} was observed in the range of 641–677 nm, there being bathochromic compared to those in dichloromethane (593–595 nm), indicating the intermolecular interactions in the solid state.

The solid-state fluorescence of 1-butyl-2-[4-(diethylamino) styryl]pyridinium dyes **17**, **27**, **28**, **29**, and **30** are indicated in Fig. 2a. The fluorescence was more intense in the order of the counter anion: $(C_4F_9SO_2)_2N$ (**30**, Φ_f = 0.16) > $(CF_2)_3(SO_2)_2N$ (**29**, 0.10) > CF_3SO_3 (**27**, 0.07), $(CF_3SO_2)_2N$ (**28**, 0.04), and Br (**17**, 0.02). The solid-state fluorescence of 1-alkyl-2-[4-(diethylamino)styryl] pyridinium bis(perfluorobutylsulfonyl)imides **25**, **26**, **27**, **30**, **32**, and **33** are also shown in Fig. 2b. The fluorescence of Et (**26**, 0.14) and Bu (**30**, 0.16) derivatives were more intense than those of Me (**25**, 0.03), Octyl (**31**, 0.05), Dodecyl (**32**, 0.03), and Octadecyl (**33**, 0.08) derivatives (Table 1).

2.3. X-ray crystallography

To understand why the solid-state fluorescence intensity of styryl dyes depends on the counter anion and the alkyl substituent on the pyridinium-nitrogen, the X-ray crystallography of **17**, **25**, and **30** was performed.

The X-ray crystallography of **17** is shown in Fig. 3. Molecules are arranged in parallel. Molecules A and B form a head-to-tail dimer with π/π interactions (top view (1)). The interplanar distance is 3.43 Å (side view). Molecule C is also packed in parallel for B. The π/π interactions are observed at the edge of *p*-(diethylamino)phenylene rings of B and C with interplanar distance 3.95 Å (top view (2) and side view). The cationic fluorophore has two short contacts with neighboring bromo anions. The distance between the α-carbon on the *N*-butyl group in the pyridinium moiety of B and bromo anion E is 3.68 Å (overview (1) and (2)). The distance between the olefinic bond and another bromo anion D is 3.85 Å. As a bromo anion is smaller than the other anions in this study, the π/π interactions is a main factor for the packing. Thus, compound **17** has consequent π/π interactions (side view).

The X-ray crystal structure of **25** is shown in Fig. 4. Molecules form a pair of head-to-tail dimers and are packed in parallel. Bis(perfluorobutylsulfonyl)imido anions are located beside the cationic fluorophores. The cationic fluorophore has three short contacts

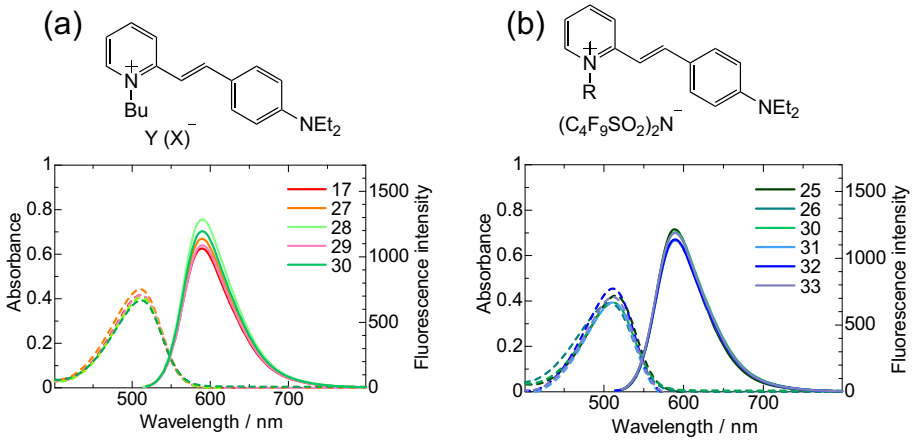

Fig. 1. UV–vis absorption and fluorescence spectra (a) change in *Y* (×) and (b) change in *R*. Measured on 1.0×10^{-5} mol dm^{-3} at 25 °C in dichloromethane. Solid and dotted lines represent fluorescence and UV–vis absorption spectra, respectively.

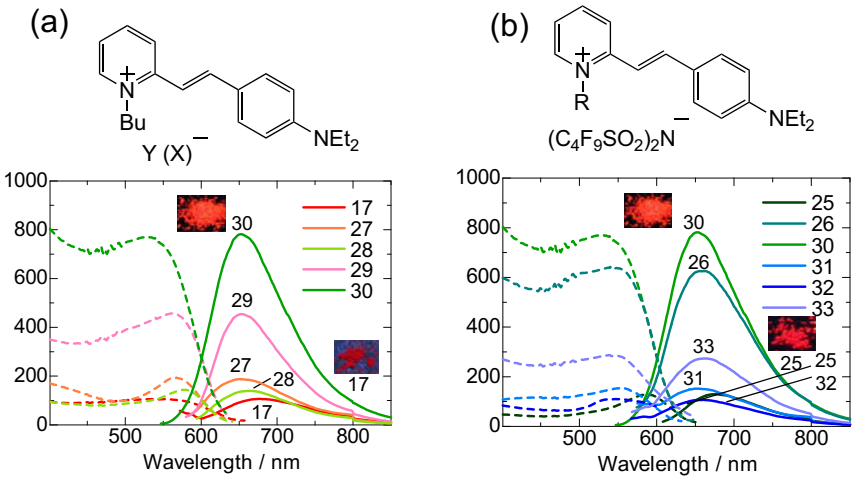

Fig. 2. Solid-state fluorescence spectra (a) change in *Y* (×) and (b) change in *R*. Solid and dotted lines represent fluorescence and excitation spectra, respectively.

with adjacent anions. The carbon atom at the 3-position on the pyridinium ring and the olefinic bond of B has interactions with one of the sulfonyl-oxygen of the anion E with length 3.42 and 3.38 Å, respectively (overview (1)). The carbon atom at the 2-position on the *p*-(diethylamino)phenylene ring of B also has interactions with one of the oxygen atom of another sulfonyl group in D with 3.53 Å (overview (1) and (2)). Molecules A and B have π/π interactions with interplanar distance 3.52 Å (top view (1) and side view). Molecules B and C also have π/π interactions with interplanar distance 3.47 Å (top view (2) and side view). The *N*-methyl group is located on the same plane to the styryl skeleton not to sterically hinder the adjacent cationic fluorophores (side view). As the result, consequent π/π interaction is observed for **25** (side view).

The single X-ray crystal structure of **30** is shown in Fig. 5. Molecules form a pair of head-to-tail dimers with π/π interactions and are packed in parallel. The interplanar distance between A and B is 3.38 Å (top view (1) and side view). Though molecules C is packed in parallel for B, the interplanar distance is 4.81 Å being too long to have π/π interactions (top view (2) and side view). Bis(perfluorobutylsulfonyl) imido anions are located beside the cationic fluorophores. Cationic fluorophore has four short contacts with adjacent anions. The α-carbon at the pyridinium ring, olefinic bond, and carbon atom at the 2-position in *p*-(diethylamino)phenylene ring of B have interactions with one of the sulfonyl-oxygen of E with distances of 3.51, 3.47, and 3.37 Å, respectively (overview (1) and (2)). The carbon atom at the 3-position in the pyridinium ring of B has interactions with imido-nitrogen of another adjacent anion D. The packing direction of the anions in **30** is different from that in **25**. In the case of **30**, the *N*-butyl group could sterically hinder the neighboring dimer units preventing π/π interactions among the units. Then, one side of perfluorobutylsulfonyl moiety can hinder the pyridinium styryl fluorophores packing in parallel. As a result, no consequent π/π interactions are observed for **30**. Compound **30** has isolated dimer-type packing (side view).

The fluorophores of styryl dyes have interactions with both the counter anions and the neighboring cationic fluorophores. A bromo anion is smaller than the other imido anions. The cationic fluorophores of **17**, **25**, and **30** have two, three, and four short contacts with anions as shown in Figs. 3–5, respectively. The cation-anion contacts (3.68 and 3.85 Å) in **17** is significantly long compared with those of **25** (3.38, 3.42, and 3.53 Å) and **30** (3.37, 3.47, 3.51, and 3.62 Å). The Coulomb interactions are inversely proportional to the square of the bond length. Thus, compounds **25** and **30** have stronger cation-anion interactions than **17**. However, **17** shows less intense fluorescence than **25** and **30**. These results suggest that the cation-anion Coulomb interactions are not the main factor affecting the fluorescence intensity in the solid state.

In the case of neutral compounds, consequent π/π interactions and intermolecular hydrogen bonding of the fluorophore reduce the solid-state fluorescence intensity. Therefore, it is quite reasonable to consider that as cationic fluorophores of **17** and **25** have consecutive π/π stacking to show weak intensity compared with **30**, which has isolated dimer-type packing.

Meanwhile, the solid-state fluorescence intensity also depends on the melting point [18]. In low-melting point compounds, the stretching, vibration, and rotation of chemical bonds can occur to accelerate the non-radiation process from S_1 state to S_0 state. The melting points of **17**, **25**, and **30** are 249, 132, and 81.6 °C, respectively. It is suspected that, in the case of **31**, **32**, and **33**, as the melting point is low (55.2–70.2 °C), the fluorescence intensity is low. Therefore, the balance between the intermolecular interactions and its melting point is important for intensely solid-state fluorescent compounds. Compounds **17**, **25**, and **30** form the dimers in the crystalline form. No emission peak was observed for these compounds beyond 800 nm, indicating no fluorescence from the eximer. Therefore, the molecular design of styryl dyes forming isolated monomer-type packing with medium melting point is required to obtain more intense solid-state fluorescent styryl dyes.

3. Conclusion

1-Butyl-2-[4-(diethylamino)styryl]pyridinium bis(perfluorobutylsulfonyl)imide exhibited a fluorescence maximum at 652 nm with the highest fluorescence quantum yield of 0.16 among any derivatives in the solid state. The X-ray crystal structure suggests that this compound has isolated dimer-type packing leading to intense solid-state fluorescence.

4. Experimental

4.1. 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

Table 1
Physical properties of pyridinium styryl dyes.

Compd	*R*	*Y* (*X*)	mp/°C	In dichloromethane[a]			Solid state		
				λ_{max}/nm (ε)	F_{max}/nm	Φ_f[b]	λ_{ex}/nm	F_{max}/nm	Φ_f[b]
17	Bu	Br	249–250	508 (41,600)	595	0.10	557	677	0.02
25	Me	$(C_4F_9SO_2)_2N$	132–133	514 (42,200)	595	0.11	588	677	0.03
26	Et	$(C_4F_9SO_2)_2N$	118–119	510 (41,600)	595	0.11	554	662	0.14
27	Bu	CF_3SO_3	152–153	510 (44,200)	593	0.12	565	652	0.07
28	Bu	$(CF_3SO_2)_2N$	121–122	512 (40,600)	594	0.12	574	665	0.04
29	Bu	$(CF_2)_3(SO_2)_2N$	140–141	512 (40,500)	594	0.12	560	654	0.10
30	Bu	$(C_4F_9SO_2)_2N$	81.6	508 (41,800)	595	0.11	529	652	0.16
31	Oct	$(C_4F_9SO_2)_2N$	70.2	512 (39,400)	593	0.11	555	651	0.05
32	Dodec	$(C_4F_9SO_2)_2N$	55.2	511 (45,500)	595	0.11	580	643	0.03
33	Octadec	$(C_4F_9SO_2)_2N$	65.4	512 (41,800)	593	0.11	548	664	0.08

[a] Measured on 1×10^{-5} mol dm^{-3} of substrate at 25 °C.
[b] Determined by a Hamamatsu Photonics Quantaurus-QY.

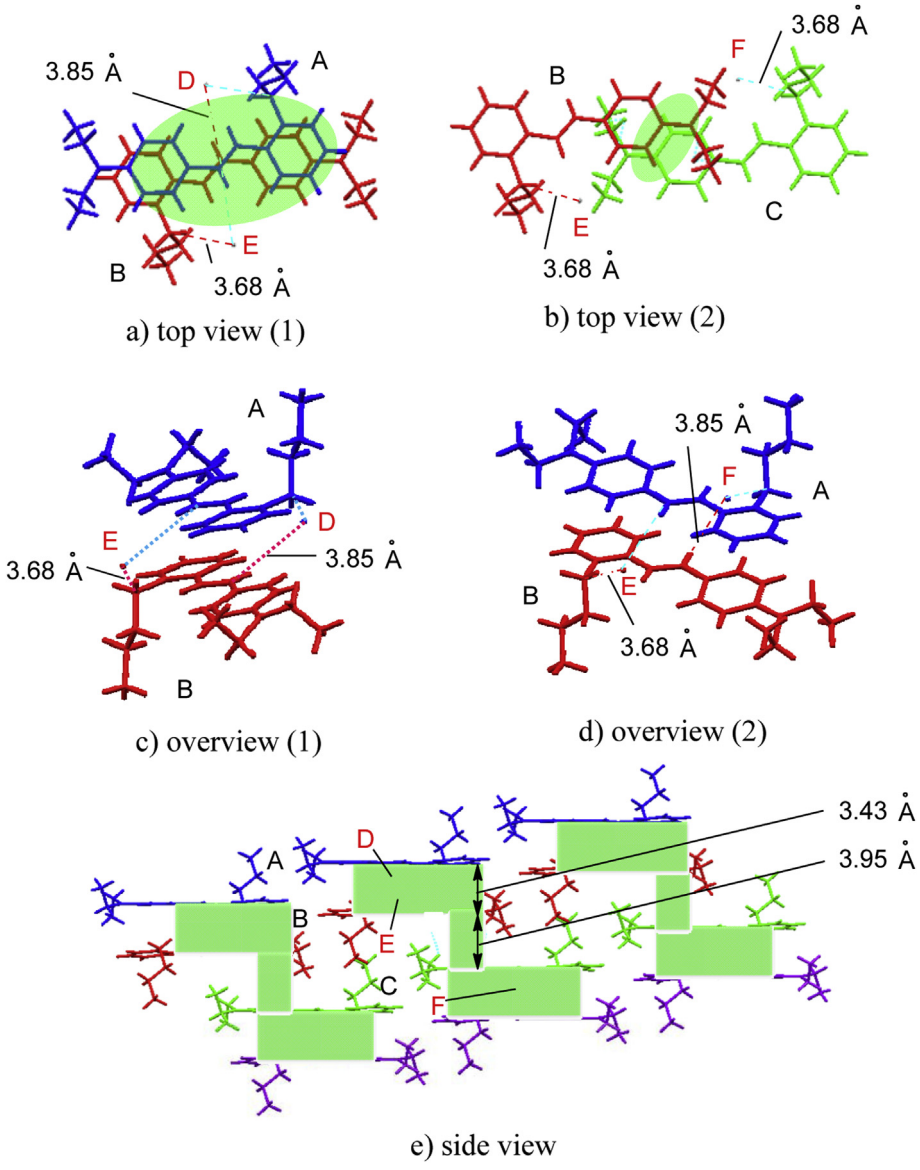

Fig. 3. Single X-ray crystallography of **17**.

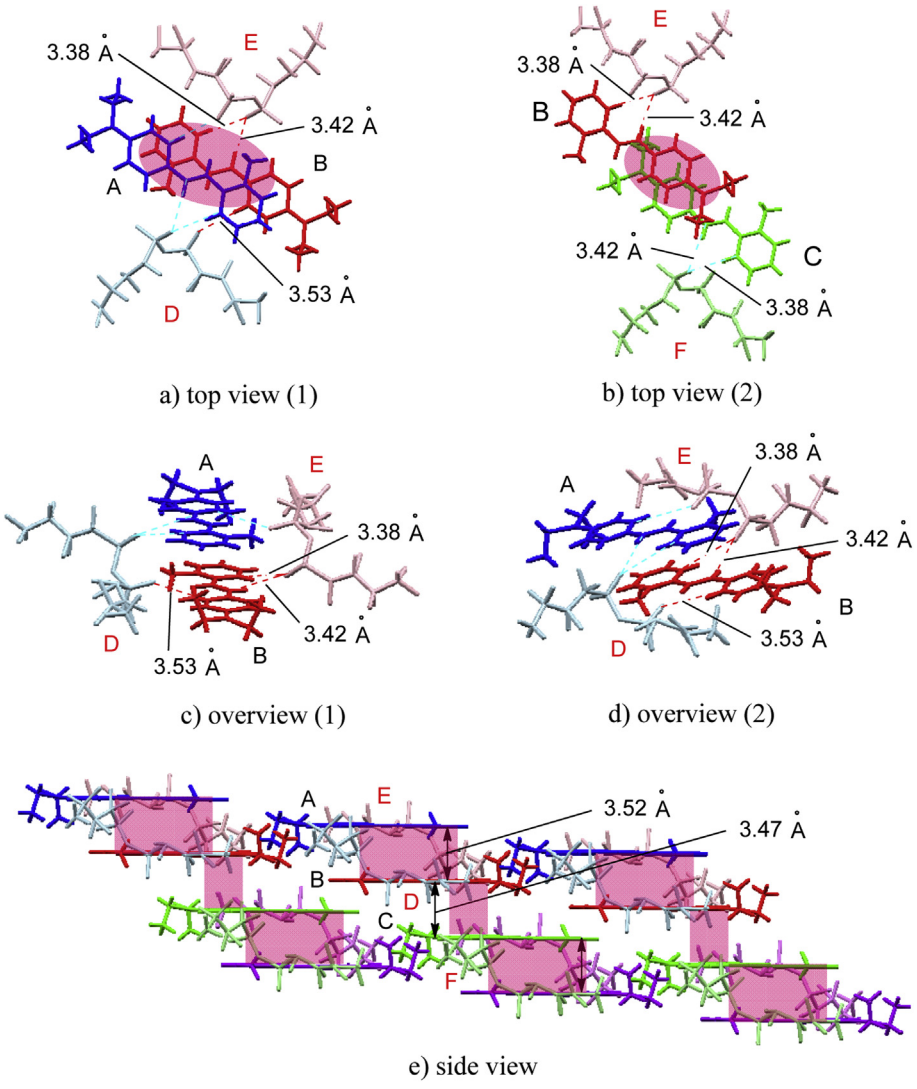

Fig. 4. Single X-ray crystallography of **25**.

were taken on Hitachi U-3500 and JASCO FP8600 spectrophotometers, respectively. Fluorescence quantum yields were measured by a Hamamatsu Photonics Quantaurus-QY.

4.2. 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-4*H*-1,3,2-dithiazine 1,1,3,3-tetraoxide (**22**), and lithium bis(perfluorobutylsulfonyl)imide (**24**) were purchased from Wako Chemical Industries, Ltd. Octadecyl iodide (**7**), lithium trifluoromethanesulfonate (**21**), and lithium bis(trifluoromethylsulfonyl)imide (**23**) were purchased from TOKYO KASEI KOGYO CO., LTD., Sigma–Aldrich Co., Ltd., and Kanto Chemical Co., Inc., respectively.

4.3. 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**, **12**, **13**: neat) was added an alkyl halide **2**–**7** (22 mmol). The mixture was refluxed (5 days) or heated (overnight). In the case of **8**, **9**, and **10**, the reaction mixture was concentrated. To the residue was added acetonitrile and poured into ether. The resulting solid was filtered and dried to give a white solid.

4.3.1. 1,2-Dimethylpyridinium iodide (***8***)

Yield 72%; mp 235–236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.96 (s, 3H), 4.54 (s, 3H), 7.91 (d, J = 7.1 Hz, 1H), 7.93 (t, J = 7.1 Hz, 1H), 8.37 (t, J = 7.1 Hz, 1H), 9.41 (d, J = 7.1 Hz, 1H).

4.3.2. 1-Ethyl-2-methylpyridinium bromide (***9***)

Yield 51%; mp 57.5–58.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.67 (t, J = 7.3 Hz, 3H), 3.06 (s, 3H), 4.97 (t, J = 7.3 Hz, 2H), 8.03 (t, J = 7.5 Hz, 1H), 8.14 (d, J = 7.5 Hz, 1H), 8.52 (t, J = 7.5 Hz, 1H), 9.63 (d, J = 7.5 Hz, 1H).

4.3.3. 1-Butyl-2-methylpyridinium bromide (***10***)

Yield 97%; mp 149–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.00 (t, J = 7.5 Hz, 3H), 1.53 (sex, J = 7.5 Hz, 2H), 1.92 (quin, J = 7.5 Hz, 2H), 2.97 (s, 3H), 4.98 (t, J = 7.5 Hz, 2H), 7.90 (d, J = 7.1 Hz, 1H), 8.00 (t, J = 7.1 Hz, 1H), 8.36 (t, J = 7.1 Hz, 1H), 9.88 (d, J = 7.1 Hz, 1H).

4.3.4. 2-Methyl-1-octylpyridinium iodide (***11***)

Yield 90%; mp 111–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.87 (t, J = 6.9 Hz, 3H), 1.20–1.55 (m, 10H), 1.96 (quin, J = 6.9 Hz, 2H), 2.98

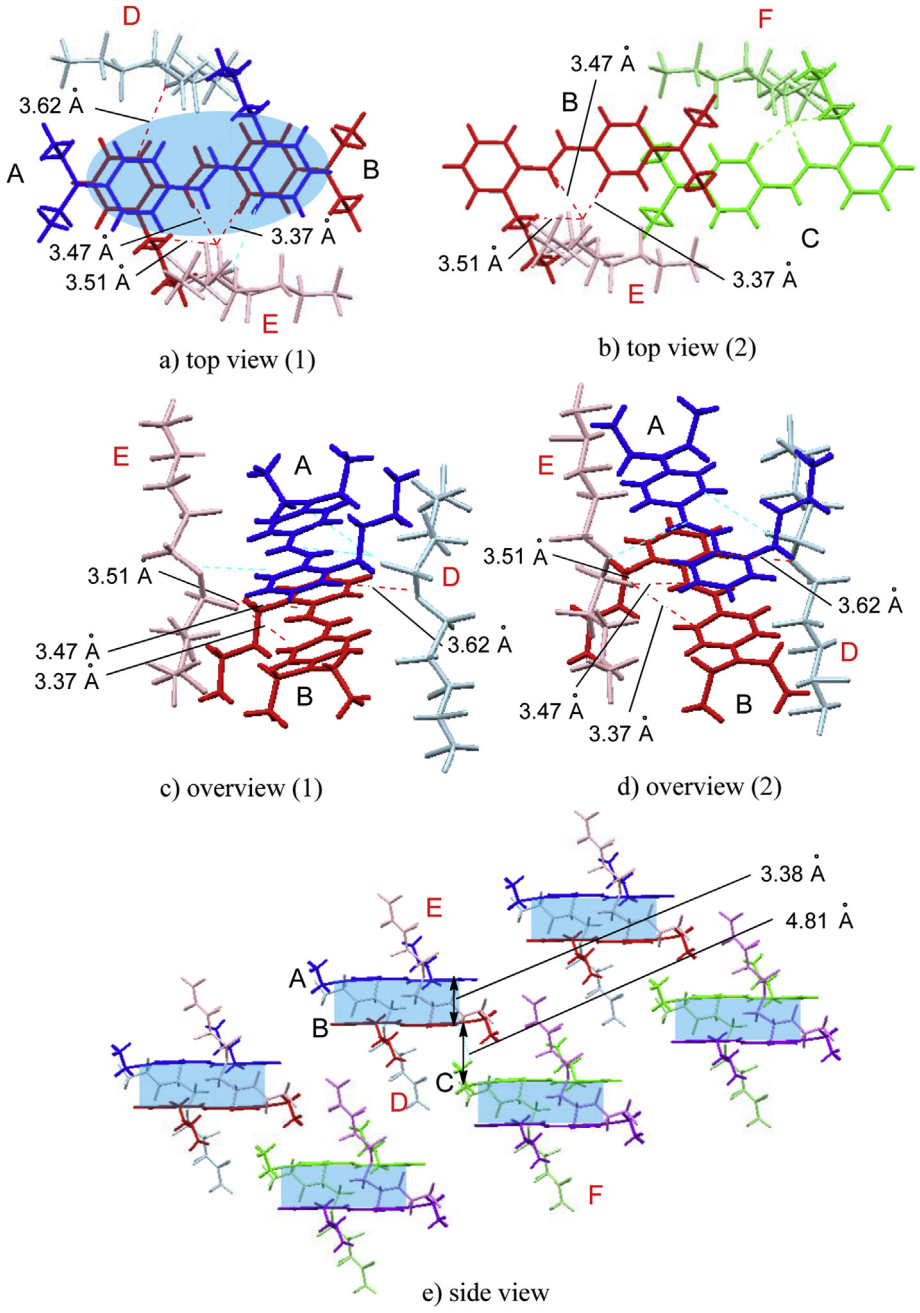

Fig. 5. Single X-ray crystallography of **30**.

(s, 3H), 4.81 (t, J = 6.9 Hz, 2H), 8.02 (t, J = 7.1 Hz, 1H), 8.14 (d, J = 7.1 Hz, 1H), 8.53 (t, J = 7.1 Hz, 1H), 9.39 (d, J = 7.1 Hz, 1H).

*4.3.5. 1-Dodecyl-2-methylpyridinium iodide (**12**)*

Yield 85%; mp 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, J = 7.3 Hz, 3H), 1.20–1.50 (m, 18H), 1.95 (quin, J = 7.3 Hz, 2H), 3.00 (s, 3H), 4.81 (t, J = 7.3 Hz, 2H), 7.90 (t, J = 7.7 Hz, 1H), 8.00 (d, J = 7.7 Hz, 1H), 8.48 (t, J = 7.7 Hz, 1H), 9.43 (d, J = 7.7 Hz, 1H).

*4.3.6. 2-Methyl-1-octadecylpyridinium iodide (**13**)*

Yield 92%; mp 130–131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, J = 7.4 Hz, 3H), 1.20–1.50 (m, 30H), 1.95 (quin, J = 7.4 Hz, 2H), 3.01 (s, 3H), 4.81 (t, J = 7.4 Hz, 2H), 8.02 (t, J = 6.8 Hz, 1H), 8.10 (d, J = 6.8 Hz, 1H), 8.51 (t, J = 6.8 Hz, 1H), 9.88 (d, J = 6.8 Hz, 1H).

*4.4. Synthesis of 1-alkyl-2-[4-(diethylamino)styryl]pyridinium halides **15**–**20***

To an ethanol solution (80 mL) of 1-alkyl-2-methylpyridinium halides **8**–**13** (8 mmol) were added 4-(diethylamino)benzaldehyde **14** (14.2 g, 8 mmol) and piperidine (a few drops). 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, MeOH–$CHCl_3$) to afford orange to red solid.

*4.4.1. 2-[4-(Diethylamino)styryl]-1-methylpyridinium iodide (**15**)*

Yield 73%; mp 228–229 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.20 (t, J = 7.1 Hz, 6H), 3.48 (q, J = 7.1 Hz, 4H), 4.32 (s, 3H), 6.75 (d, J = 9.3 Hz, 2H), 7.14 (d, J = 15.6 Hz, 1H), 7.57 (t, J = 7.0 Hz, 1H), 7.64 (d, J = 9.3 Hz, 2H), 7.82 (d, J = 15.6 Hz, 1H), 8.24 (t, J = 7.0 Hz, 1H),

8.34 (d, J = 7.0 Hz, 1H), 8.56 (d, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 12.6 (2C), 44.7 (2C), 47.2, 108.3, 111.6 (2C), 121.2, 122.8, 123.7, 131.7 (2C), 142.8, 145.6, 145.8, 150.7, 154.0; IR (KBr) $\tilde{\nu}$ = 1593, 1160, 1526, 1193; Anal. calcd for $C_{18}H_{23}IN_2$: C, 54.83; H, 5.88; N, 7.10%. Found: C, 54.41, H, 5.75, N, 7.07%.

4.4.2. 2-[4-(Diethylamino)styryl]-1-ethylpyridinium bromide (**16**)

Yield 27%; mp 195–196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.22 (t, J = 7.2 Hz, 6H), 1.64 (t, J = 7.2 Hz, 3H), 3.44 (q, J = 7.2 Hz, 4H), 5.03 (q, J = 7.2 Hz, 2H), 6.69 (d, J = 8.9 Hz, 2H), 7.02 (d, J = 15.4 Hz, 1H), 7.59 (d, J = 8.9 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.64 (d, J = 15.4 Hz, 1H), 8.17 (d, J = 7.2 Hz, 1H), 8.20 (t, J = 7.2 Hz, 1H), 8.52 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 12.5 (2C), 15.6, 44.6 (2C), 53.6, 108.2, 111.4 (2C), 121.2, 123.4, 131.3 (2C), 143.0, 145.0, 145.4, 145.5, 150.4, 152.8; IR (KBr) $\tilde{\nu}$ = 1590, 1160, 1526, 1194; Anal. calcd for $C_{19}H_{25}BrN_2$: C, 63.16; H, 6.97; N, 7.75%. Found: C, 63.48, H, 7.24, N, 7.45%.

4.4.3. 1-Butyl-2-[4-(diethylamino)styryl]pyridinium bromide (**17**)

Yield 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.98 (t, J = 7.6 Hz, 3H), 1.22 (t, J = 7.2 Hz, 6H), 1.54 (sex, J = 7.6 Hz, 2H), 1.95 (quin, J = 7.6 Hz, 2H), 3.44 (q, J = 7.2 Hz, 4H), 5.00 (t, J = 7.6 Hz, 2H), 6.70 (d, J = 9.2 Hz, 2H), 6.97 (d, J = 15.1 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.64 (d, J = 9.2 Hz, 2H), 7.84 (d, J = 15.1 Hz, 1H), 8.08 (d, J = 7.2 Hz, 1H), 8.15 (t, J = 7.2 Hz, 1H), 9.69 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 12.6 (2C), 13.7, 19.5, 32.0, 44.7 (2C), 57.8, 108.4, 111.5 (2C), 121.4, 123.1, 124.6, 131.3 (2C), 143.3, 145.3, 145.5, 150.4, 152.9; IR (KBr) $\tilde{\nu}$ = 1590, 1155, 1525, 1190; Anal. calcd for $C_{21}H_{29}BrN_2$: C, 64.78; H, 7.51; N, 7.19%. Found: C, 64.48; H, 7.24; N, 7.45%.

4.4.4. 2-[4-(Diethylamino)styryl]-1-octylpyridinium iodide (**18**)

Yield 75%; mp 173–175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.83 (t, J = 7.6 Hz, 3H), 1.10–1.50 (m, 16H), 1.91 (quin, J = 7.6 Hz, 2H), 3.42 (q, J = 7.2 Hz, 4H), 4.83 (t, J = 7.6 Hz, 2H), 6.63 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 15.6 Hz, 1H), 7.58 (d, J = 8.9 Hz, 2H), 7.60 (d, J = 6.4 Hz, 1H), 7.70 (d, J = 15.6 Hz, 1H), 8.23 (t, J = 6.4 Hz, 1H), 8.27 (t, J = 6.4 Hz, 1H), 9.12 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 12.6 (2C), 14.0, 22.4, 26.0, 28.9, 29.0, 29.8, 31.6, 44.6 (2C), 58.2, 108.1, 111.4 (2C), 121.2, 123.0, 124.6, 131.3 (2C), 143.1, 144.7, 145.4, 150.3, 152.8; IR (KBr) $\tilde{\nu}$ = 1591, 1156, 1522, 1191; Anal. calcd for $C_{25}H_{37}IN_2$: C, 60.97; H, 7.57; N, 5.69%. Found: C, 60.59; H, 7.74; N, 5.60%.

4.4.5. 2-[4-(Diethylamino)styryl]-1-dodecylpyridinium iodide (**19**)

Yield 87%; mp 270–271 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.85 (t, J = 7.6 Hz, 3H), 0.98 (t, J = 7.3 Hz, 6H), 1.11–1.65 (m, 18H), 1.91 (quin, J = 7.6 Hz, 2H), 3.35 (q, J = 7.3 Hz, 4H), 4.55 (t, J = 7.6 Hz, 2H), 6.65 (d, J = 8.9 Hz, 2H), 6.85 (d, J = 15.6 Hz, 1H), 7.49 (d, J = 8.9 Hz, 2H), 7.54 (d, J = 6.0 Hz, 1H), 7.59 (d, J = 15.6 Hz, 1H), 7.54 (t, J = 6.0 Hz, 1H), 8.10 (t, J = 6.0 Hz, 1H), 8.50 (d, J = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 12.5 (2C), 14.0, 21.6, 22.0, 22.5, 26.0, 29.0, 29.2, 29.4, 29.8, 31.7, 44.3, 44.5 (2C), 58.3, 108.1, 111.4 (2C), 121.1, 123.1, 124.6, 131.3 (2C), 143.1, 144.5, 145.4, 150.3, 152.9; IR (KBr) $\tilde{\nu}$ = 1590, 1156, 1524, 1190; Anal. calcd for $C_{29}H_{45}IN_2$: C, 63.49; H, 8.27; I, 23.13; N, 5.11%. Found: C, 63.18, H, 8.06; N, 5.26%.

4.4.6. 2-[4-(Diethylamino)styryl]-1-octadecylpyridinium iodide (**20**)

Yield 72%; mp 183–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.87 (t, J = 7.2 Hz, 3H), 1.19–1.36 (m, 34H), 1.45 (quin, J = 7.2 Hz, 2H), 1.92 (quin, J = 7.2 Hz, 2H), 3.43 (q, J = 7.0 Hz, 4H), 4.84 (t, J = 7.2 Hz, 2H), 6.67 (d, J = 8.7 Hz, 2H), 6.97 (d, J = 15.1 Hz, 1H), 7.60 (t, J = 7.3 Hz, 1H), 7.65 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 15.1 Hz, 1H), 8.29 (t, J = 7.3 Hz, 1H), 8.39 (d, J = 7.3 Hz, 1H), 9.09 (d, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 12.1, 14.2, 22.7 (2C), 26.2, 29.2, 29.4 (2C), 29.6, 29.7 (2C), 29.8 (5C), 30.0, 32.0 (2C), 44.8 (2C), 58.4, 108.3, 111.6 (2C), 121.4, 123.1, 124.9, 131.6 (2C), 143.2, 144.8, 145.6, 150.5, 153.0; IR (KBr) $\tilde{\nu}$ = 2922, 1590, 1557, 1525, 1193; Anal. calcd for $C_{35}H_{57}IN_2$: C, 66.44; H, 9.08; N, 4.43%. Found: C, 66.16; H, 8.91; N, 4.03%.

4.5. Synthesis of 1-alkyl-2-[4-(diethylamino)styryl]pyridinium dyes **25**–**33**

To a water–acetone (2:1) mixed solution (30 mL) of 1-alkyl-2-[4-(diethylamino)styryl]pyridinium halides **15**–**20** (1 mmol) was added a lithium salt **21**–**24** (1.25 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 (Al_2O_3, THF/MeOH = 5/1) to provide orange to red solid or liquid.

4.5.1. 2-[4-(Diethylamino)styryl]-1-methylpyridinium bis(perfluorobutylsulfonyl)imide (**25**)

Yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.21 (t, J = 7.1 Hz, 6H), 3.34 (q, J = 7.1 Hz, 4H), 4.26 (s, 3H), 6.67 (d, J = 8.9 Hz, 2H), 6.89 (d, J = 15.6 Hz, 1H), 7.47 (t, J = 6.8 Hz, 1H), 7.53 (d, J = 8.9 Hz, 2H), 7.58 (d, J = 15.6 Hz, 1H), 8.07 (t, J = 6.8 Hz, 1H), 8.10 (d, J = 6.8 Hz, 1H), 8.46 (d, J = 6.8 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, ext. $CFCl_3$) δ = −125.8 (4F), −121.0 (4F), −112.7 (4F), −80.7 (6F); IR (KBr) $\tilde{\nu}$ = 1592, 1562, 1526, 1365, 1228, 1194, 1177, 1155; Anal. calcd for $C_{26}H_{23}F_{18}N_3O_4S_2$: C, 36.84; H, 2.74; N, 4.96%. Found: C, 36.54; H, 2.93; N, 4.95%.

4.5.2. 2-[4-(Diethylamino)styryl]-1-ethylpyridinium bis(perfluorobutylsulfonyl)imide (**26**)

Yield 61%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.23 (t, J = 7.2 Hz, 6H), 1.61 (t, J = 7.3 Hz, 3H), 3.45 (q, J = 7.2 Hz, 4H), 4.66 (q, J = 7.3 Hz, 2H), 6.69 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 15.6 Hz, 1H), 7.53 (d, J = 8.7 Hz, 2H), 7.56 (t, J = 6.9 Hz, 1H), 7.59 (d, J = 15.6 Hz, 1H), 8.08 (d, J = 6.9 Hz, 1H), 8.14 (t, J = 6.9 Hz, 1H), 8.57 (d, J = 6.9 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, ext. $CFCl_3$) δ = −125.8 (4F), −120.9 (4F), −112.7 (4F), −80.7 (6F); IR (KBr) $\tilde{\nu}$ = 1591, 1560, 1526, 1355, 1236, 1190, 1154; Anal. calcd for $C_{27}H_{25}F_{18}N_3O_4S_2$: C, 37.64; H, 2.92; N, 4.88%. Found: C, 37.33; H, 3.06; N, 4.89%.

4.5.3. 1-Butyl-2-[4-(diethylamino)styryl]pyridinium trifluoromethanesulfonate (**27**)

Yield 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.01 (t, J = 7.5 Hz, 3H), 1.23 (t, J = 7.1 Hz, 6H), 1.47 (sex, J = 7.5 Hz, 2H), 1.92 (quin, J = 7.5 Hz, 2H), 3.45 (q, J = 7.1 Hz, 4H), 4.58 (t, J = 7.5 Hz, 2H), 6.70 (d, J = 9.2 Hz, 2H), 6.88 (d, J = 15.6 Hz, 1H), 7.50 (d, J = 9.2 Hz, 2H), 7.56 (t, J = 7.1 Hz, 1H), 7.59 (d, J = 15.6 Hz, 1H), 8.07 (d, J = 7.1 Hz, 1H), 8.14 (t, J = 7.1 Hz, 1H), 8.54 (d, J = 7.1 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, ext. $CFCl_3$) δ = −78.1 (3F); IR (KBr) $\tilde{\nu}$ = 1594, 1564, 1526, 1272, 1263, 1031; Anal. calcd for $C_{22}H_{29}F_3N_2O_3S$: C, 57.63; H, 6.37; N, 6.11%. Found: C, 57.39; H, 6.12; N, 6.26%.

4.5.4. 1-Butyl-2-[4-(diethylamino)styryl]pyridinium bis(trifluoromethylsulfonyl)imide (**28**)

Yield 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.01 (t, J = 7.5 Hz, 3H), 1.23 (t, J = 7.1 Hz, 6H), 1.47 (sex, J = 7.5 Hz, 2H), 1.92 (quin, J = 7.5 Hz, 2H), 3.45 (q, J = 7.1 Hz, 4H), 4.58 (t, J = 7.5 Hz, 2H), 6.70 (d, J = 9.2 Hz, 2H), 6.88 (d, J = 15.6 Hz, 1H), 7.50 (d, J = 9.2 Hz, 2H), 7.58 (t, J = 7.0 Hz, 1H), 7.58 (d, J = 15.6 Hz, 1H), 8.07 (d, J = 7.0 Hz, 1H), 8.14 (t, J = 7.0 Hz, 1H), 8.55 (d, J = 7.0 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, ext. $CFCl_3$) δ = −78.6 (6F); IR (KBr) $\tilde{\nu}$ = 1591, 1560, 1527, 1354, 1203, 1191; Anal. calcd for $C_{23}H_{29}F_6N_3O_4S_2$: C, 46.85; H, 4.96; N, 7.13%. Found: C, 46.67; H, 4.88; N, 7.18%.

4.5.5. 1-Butyl-2-[4-(diethylamino)styryl]pyridinium 4,4,5,5,6,6-hexafluorodihydro-4H-1,3,2-dithiazine 1,1,3,3,-tetraoxide (**29**)

Yield 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.01 (t, J = 7.5 Hz, 3H), 1.23 (t, J = 7.1 Hz, 6H), 1.47 (sex, J = 7.5 Hz, 2H), 1.92 (quin, J = 7.5 Hz,

2H), 3.45 (q, $J = 7.1$ Hz, 4H), 4.57 (t, $J = 7.5$ Hz, 2H), 6.70 (d, $J = 8.9$ Hz, 2H), 6.88 (d, $J = 15.6$ Hz, 1H), 7.51 (d, $J = 8.9$ Hz, 2H), 7.56 (t, $J = 7.0$ Hz, 1H), 7.58 (d, $J = 15.6$ Hz, 1H), 8.08 (d, $J = 7.0$ Hz, 1H), 8.14 (t, $J = 7.0$ Hz, 1H), 8.48 (d, $J = 7.0$ Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, ext. $CFCl_3$) $\delta = -127.6$ (2F), −121.1 (4F); IR (KBr) $\tilde{\nu} = 1591, 1560, 1526, 1358, 1193, 1155$; Anal. calcd for $C_{24}H_{29}F_6N_3O_4S_2$: C, 47.91; H, 4.86; N, 6.98%. Found: C, 47.54; H, 4.75; N, 6.88%.

4.5.6. 1-Butyl-2-[4-(diethylamino)styryl]pyridinium bis(perfluorobutylsulfonyl)imide (**30**)

Yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.00$ (t, $J = 7.4$ Hz, 3H), 1.22 (t, $J = 7.1$ Hz, 6H), 1.47 (sex, $J = 7.4$ Hz, 2H), 1.90 (quin, $J = 7.4$ Hz, 2H), 3.45 (q, $J = 7.1$ Hz, 4H), 4.58 (t, $J = 7.4$ Hz, 2H), 6.70 (d, $J = 9.2$ Hz, 2H), 6.88 (d, $J = 15.6$ Hz, 1H), 7.50 (d, $J = 9.2$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.57 (d, $J = 15.6$ Hz, 1H), 8.07 (d, $J = 7.2$ Hz, 1H), 8.13 (t, $J = 7.2$ Hz, 1H), 8.55 (d, $J = 7.2$ Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, ext. $CFCl_3$) $\delta = -125.9$ (4F), −121.0 (4F), −112.8 (4F), −80.7 (6F); IR (KBr) ν 1591, 1560, 1528, 1360, 1237, 1192, 1168 cm^{-1}; IR: $\tilde{\nu} = 1560, 1522, 1507, 1362, 1355, 1239, 1198$; Anal. calcd for $C_{29}H_{29}F_{18}N_3O_4S_2$: C, 39.15; H, 3.29; N, 4.72%. Found: C, 39.03; H, 3.33; N, 4.74%.

4.5.7. 2-[4-(Diethylamino)styryl]-1-octylpyridinium bis(perfluorobutylsulfonyl)imide (**31**)

Yield 91%; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.86$ (t, $J = 7.6$ Hz, 3H), 1.10–1.53 (m, 16H), 1.96 (quin, $J = 7.6$ Hz, 2H), 3.45 (q, $J = 7.2$ Hz, 4H), 5.01 (t, $J = 7.6$ Hz, 2H), 6.70 (d, $J = 8.9$ Hz, 2H), 6.98 (d, $J = 15.6$ Hz, 1H), 7.54 (d, $J = 8.9$ Hz, 2H), 7.58 (d, $J = 6.4$ Hz, 1H), 7.67 (d, $J = 15.6$ Hz, 1H), 8.10 (t, $J = 6.4$ Hz, 1H), 8.18 (t, $J = 6.4$ Hz, 1H), 9.76 (d, $J = 6.4$ Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, ext. $CFCl_3$) $\delta = 125.8$ (4F), −121.9 (4F), −112.7 (4F), −80.7 (6F); IR (KBr) $\tilde{\nu} = 1560, 1522, 1507, 1362, 1355, 1239, 1198$; Anal. calcd for $C_{33}H_{37}F_{18}N_3O_4S_2$: C, 41.92; H, 3.94; N, 4.44%. Found: C, 42.20; H, 4.12; N, 4.10%.

4.5.8. 2-[4-(Diethylamino)styryl]-1-dodecylpyridinium bis(perfluorobutylsulfonyl)imide (**32**)

Yield 88%; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.87$ (t, $J = 7.2$ Hz, 3H), 1.11–1.43 (m, 24H), 1.91 (quin, $J = 7.6$ Hz, 2H), 3.44 (q, $J = 7.2$ Hz, 4H), 4.56 (t, $J = 7.2$ Hz, 2H), 6.69 (d, $J = 9.2$ Hz, 2H), 6.87 (d, $J = 15.4$ Hz, 1H), 7.50 (d, $J = 9.2$ Hz, 2H), 7.55 (d, $J = 6.8$ Hz, 1H), 7.58 (d, $J = 15.4$ Hz, 1H), 8.11 (t, $J = 6.8$ Hz, 1H), 8.15 (t, $J = 6.8$ Hz, 1H), 8.52 (d, $J = 6.8$ Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, ext. $CFCl_3$) $\delta = -125.9$ (4F), −121.0 (4F), −112.8 (4F), −80.7 (6F); IR (KBr) $\tilde{\nu} = 1592, 1560, 1526, 1357, 1237, 1191, 1154$; Anal. calcd for $C_{37}H_{45}F_{18}N_3O_4S_2$: C, 44.36; H, 4.53; N, 4.19%. Found: C, 44.37; H, 4.46; N, 4.21%.

4.5.9. 2-[4-(Diethylamino)styryl]-1-octadecylpyridinium bis(perfluorobutylsulfonyl)imide (**33**)

Yield 68%; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 0.88$ (t, $J = 7.3$ Hz, 3H), 1.21–1.42 (m, 36H), 1.92 (quin, $J = 7.3$ Hz, 2H), 3.45 (q, $J = 7.0$ Hz, 4H), 4.56 (t, $J = 7.3$ Hz, 2H), 6.69 (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 15.6$ Hz, 1H), 7.50 (d, $J = 8.7$ Hz, 2H), 7.56 (d, $J = 6.8$ Hz, 1H), 7.58 (d, $J = 15.6$ Hz, 1H), 8.08 (d, $J = 6.8$ Hz, 1H), 8.15 (t, $J = 6.8$ Hz, 1H), 8.54 (d, $J = 6.8$ Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$, ext. $CFCl_3$) $\delta = -125.8$ (4F), −120.9 (4F), −112.7 (4F), −80.7 (6F); IR (KBr) $\tilde{\nu} = 2927, 1590, 1560, 1527, 1355, 1237, 1154$; Anal. calcd for $C_{43}H_{57}F_{18}N_3O_4S_2$: C, 47.55; H, 5.29; N, 3.87%. Found: C, 47.47; H, 5.16; N, 3.83%.

4.6. Single X-ray crystallography of **17**, **25**, and **30**

Single crystals were obtained by diffusion method using dichloromethane and hexane. The structure was solved by direct methods and refined by fill-matrix least-squares calculations. These data can be obtained free of charge from The Cambridge Crystallographic Data Cetre via www.ccdc.cam.ac.uk/data_request/cif. CCDC 929916 (**17**), CCDC 929917 (**25**), and CCDC 929915 (**30**). Crystal data for **17**: $C_{21}H_{29}BrN_2$, $Mw = 389.37$, triclinic, P-1, $Z = 2$, $a = 10.003(4)$, $b = 10.396(4)$, $c = 11.409(4)$ Å, $\alpha = 62.753(11)$, $\beta = 73.534(16)$, $\gamma = 90.52(2)^\circ$, $D_{calcd} = 1.296$ g cm^{-3}, $T = 296$ K, $F(000) = 408$, $\mu = 2.064$ mm^{-1}, 8268 reflections were corrected, 4478 unique ($R_{int} = 0.0276$), 220 parameters, $R_1 = 0.1254$, $wR_2 = 0.3794$, GOF 1.627, refinement on F^2. Crystal data for **25**: $C_{26}H_{23}F_{18}N_3O_4S_2$, $Mw = 847.58$, monoclinic, $P2_1/n$, $Z = 4$, $a = 10.605(12)$, $b = 11.547(13)$, $c = 28.59(3)$ Å, $\beta = 92.410(16)^\circ$, $D_{calcd} = 1.609$ g cm^{-3}, $T = 293$ K, $F(000) = 1704$, $\mu = 2.8480$ cm^{-1}, 32,349 reflections were corrected, 8052 unique ($R_{int} = 0.0503$), 677 parameters, $R_1 = 0.0961$, $wR_2 = 0.3317$, GOF 1.051, refinement on F^2. Crystal data for **30**: $C_{29}H_{29}F_{18}N_3O_4S_2$, $Mw = 889.67$, triclinic, P−1, $Z = 2$, $a = 11.450(5)$, $b = 13.101(5)$, $c = 14.163$ Å, $\alpha = 62.914(11)$, $\beta = 75.447(15)$, $\gamma = 85.904(17)^\circ$, $D_{calcd} = 1.616$ g cm^{-3}, $T = 296$ K, $F(000) = 900$, $\mu = 0.277$ mm^{-1}, 14,849 reflections were corrected, 8286 unique ($R_{int} = 0.0364$), 647 parameters, $R_1 = 0.0810$, $wR_2 = 0.1229$, GOF 1.167, refinement on F^2.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.07.026.

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