Dyes and Pigments 99 (2013) 916–923

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Solid-state fluorescence of pyridinium styryl dyes

Masaki Matsui [a,*], Kohtaro Ooiwa [a], Ayumi Okada [a], Yasuhiro Kubota [a], Kazumasa Funabiki [a], Hiroyasu Sato [b]

[a] *Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan*
[b] *X-ray Research Laboratory, Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666, Japan*

ARTICLE INFO

Article history:
Received 3 June 2013
Received in revised form
18 July 2013
Accepted 19 July 2013
Available online 2 August 2013

Keywords:
Solid-state fluorescence
Styryl dyes
Counter anion
π/π-interactions
Single X-ray crystallography
Cationic dyes

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

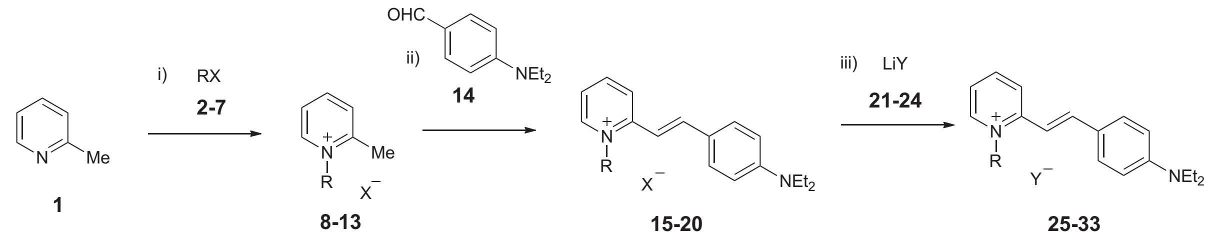
The UV–vis absorption and fluorescence spectra of **17** and **25**–**33** in dichloromethane are shown in Fig. 1. The absorption maximum (λ_{max}) was observed at around 510 nm with a molar absorption coefficient (ε) in the range of 39,400 to 45,500 mol^{-1} dm^3 cm^{-1}. The fluorescence maximum (F_{max}) 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

---

* Corresponding author.
E-mail address: matsuim@gifu-u.ac.jp (M. Matsui).

0143-7208/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.dyepig.2013.07.026



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**, $\Phi_f = 0.16$) > $(CF_2)_3(SO_2)_2N$ (**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

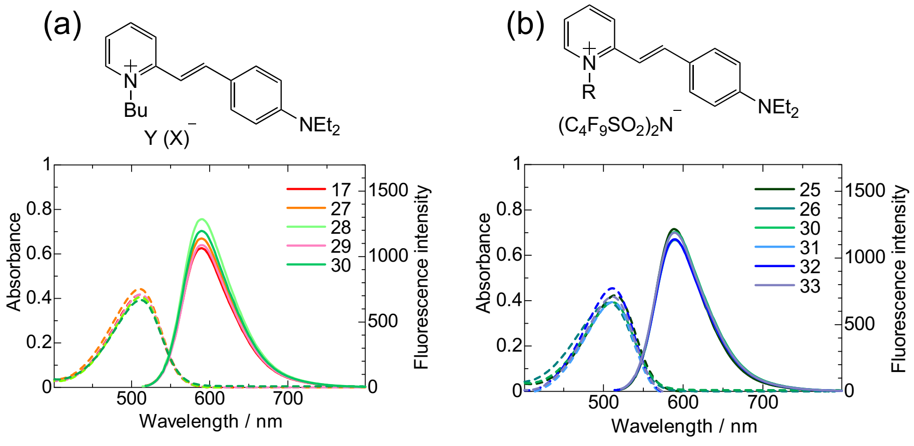


Fig. 1. UV–vis absorption and fluorescence spectra (a) change in *Y* (×) and (b) change in *R*. Measured on 1.0 × 10^{-5} mol dm^{-3} at 25 °C in dichloromethane. Solid and dotted lines represent fluorescence and UV–vis absorption spectra, respectively.