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Solid-state fluorescence of squarylium dyes

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ABSTRACT

An *N*-butyl indolenine squarylium dye could include toluene and *p*-xylene and exhibited the solid-state fluorescence in near-infrared region (F_{max}=761 nm) in crystalline form due to inhibition of π/π-interactions between the fluorophores.

1. Introduction

Solid-state fluorescent compounds have potential applications for emitters in OLED,[1] solid dye laser,[2] and sensors.[3] However, the fluorescence intensity in the solid state is generally low due to stronger interactions in the condensed and solid state. To improve this point, introduction of bulky substituent(s) into the fluorophores[4] and preparing the fluorophores enclathrating guest molecule(s) are considerable. In the latter case, the solid-state fluorescence intensity depends on the combination between the fluorophores and guest molecules. For example, in the cases of naphthooxazoles enclathrating DMSO, piperidine, morpholine, and acetone[5] and tripodal naphthalene derivative including picric acid,[6] the solid-state fluorescence intensity decreases. Meanwhile, in the cases of imidazo[4,5-*a*]naphthalenes,[7] phenanthro[9,10-*d*]imidazoles,[8] 2-(4-cyanophenyl)-4-[4-(diethylamino)phenyl]-3*H*-imidazo[4,5-*a*]naphthalenes,[9] benzo[*b*]naphtho[1,2-*d*]furan-6-one,[10] imidazoanthraquinol,[11] 2-(9-anthryl)phenanthroimid-azoles,[12] fluorenones,[13] and benzofurano[3,2-*b*]naphthoquinols,[14] enclathrating guest organic molecules could enhance the solid-state fluorescence intensity. Squarylium (SQ) dyes are important compounds showing the absorption maximum (λ_{max}) in red to near-infrared region. SQ dyes have potential applications for sensitizers in photovoltaic devices,[15] photo-conducting materials,[16] near-infrared absorbing dyes,[17] and biological analysis.[18] We considered that when SQ dyes showed solid-state fluorescence, its fluorescence maximum (F_{max}) must be observed in red to near-infrared region. To our knowledge, the most bathochromic solid-state F_{max} has been reported for 9-dibutylamino-6-{perfluoro[4-methyl-3-(1-methylethyl)-2-penten]-2-oxy}benzo[*a*]phenoxazin-5-one at 719 nm.[19] We report herein that the enclathrated SQ dyes exhibit solid-state fluorescence at near-infrared region.

2. Results and discussion

2.1. Synthesis of SQ dyes

Indolenine SQ dyes **13**–**19** were synthesized as shown in Scheme 1. 2,3,3-Trimethylindolenine (**1**) was allowed to react with alkyl iodides **2**–**6** to give *N*-alkylindolenium iodides **7**–**11**, followed by the reaction with squaric acid (**12**) to afford **13**–**16** and **19**. The indolenine SQ dyes **13** and **15** are known compounds.

2.2. Physical properties of SQ dyes

Compounds **13**, **14**, **15**, **16**, and **19** were recrystallized from ethanol. Interestingly, when compound **16** was recrystallized from toluene and *p*-xylene, the 1:1 enclathrated products **17** and **18**, respectively, were obtained. The TG–DTA measurements and pictures of **16**, **17**, and **18** are shown in Fig. 1. Compound **16** showed endothermic peak at 261 °C, corresponding to its melting point. In the case of **17** and **18**, the endothermic peak, together with decrease of one molar amount of the guest molecule, was observed at 119 and 102 °C, respectively. The ^{1}H NMR spectra of **16**, **17**, and **18**, shown in Supplementary data (Figs. S1, S2, and S3), indicating the

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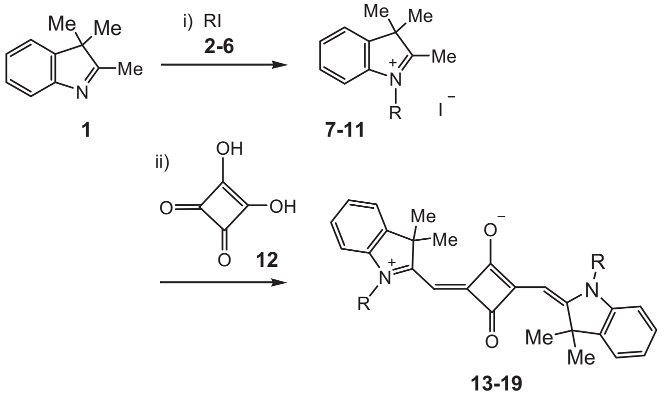

Compd	R
2	Me
3	Pr
4	*i*-Pr
5	Bu
6	Oct

Compd	R^1	R^2
7	Me	
8	Pr	
9	*i*-Pr	
10	Bu	
11	Oct	

Compd	R	
13	Me	
14	Pr	
15	*i*-Pr	
16	Bu	
17	Bu	toluene enclathrated
18	Bu	*p*-xylene enclathrated
19	Oct	

Scheme 1. Reagents and conditions: (i) **1** (30 mmol), **2**–**6** (100 mmol), MeCN, reflux, 1–2 days, (ii) **7**–**11** (1.5 mmol), **12** (3.3 mmol), BuOH/C_6H_6 (4:1), quinoline, reflux, 1–2 days.

presence of one molar amount of the guest molecule in the clathrate crystals.

Interestingly, the enclathrated products **17** and **18** show golden shade with cubic crystalline whereas the non-enclathrated derivative **16** dark-green needle crystalline. No clathrated products of **16** were obtained for benzene, *o*-xylene, *m*-xylene, ethylbenzene, ethanol, chloroform, DMF, and pyridine. No toluene-enclathrated derivative was obtained for **13**, **14**, **15**, and **19**. Thus, toluene and *p*-xylene enclathrated products were obtained only for the *N*-butyl SQ derivative **16**.

2.3. UV–vis absorption and fluorescence spectra of SQ dyes

The UV–vis absorption and fluorescence spectra of **13**–**16** and **19** in chloroform are shown in Fig. 2. The results are also listed in Table 1. These SQ dyes showed absorption maximum (λ_{max}) at around 636 nm. The molar absorption coefficients (ε) were observed in the range of 343,000 to 381,000 $dm^3\,mol^{-1}\,cm^{-1}$. The F_{max} was observed at around 646 nm. No remarkable difference in the fluorescence quantum yield (Φ_f) was observed among **13** (0.17), **14** (0.25), **15** (0.16), **16** (0.28), and **19** (0.27).

The reflection spectra of **16** given in Kubelka-Munk units are shown in Fig. 3. The spectra showed the reflection maximum at around 630 nm. Therefore, the excitation maximum (λ_{ex}) of solid-state SQ dyes was estimated to be 630 nm.

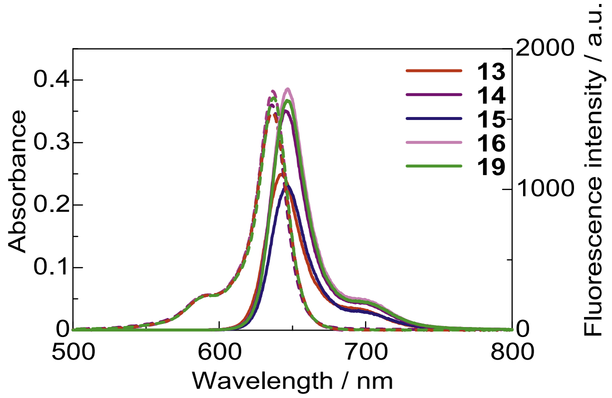

Fig. 2. UV–vis absorption and fluorescence spectra of **13**–**16** and **19** (1×10^{-6} mol dm^{-3}) in chloroform at 25 °C.

The solid-state fluorescence spectra of **13**–**19** are indicated in Fig. 4. The solid-state fluorescence was measured in the crystalline form. No solid-state fluorescence was observed for **13**–**16** and **19**. However, interestingly, the enclathrated derivatives **17** and **18** exhibited the F_{max} at 761 nm with Φ_f 0.02. After heating the toluene-enclathrated SQ dye **17** at 120 °C for 120 min, the color of the crystal changed from gold to dark green and no solid-state fluorescence was observed. The picture and solid-state fluorescence spectra before and after heating are shown in Supplementary data (Figs. S4 and S5).

2.4. Single X-ray crystallography of SQ dyes

To understand why compound **17** exhibited fluorescence in the crystalline form, the single X-ray crystallography of **16** and **17** was performed.

Table 1
UV–vis absorption and fluorescence spectra of **13**–**19**

Compd	In chloroform			Solid state	
	λ_{max} (ε)/nm[a]	F_{max}/nm[a]	Φ_f[b]	F_{max}/nm[c]	Φ_f[b]
13	633 (348,000)	643	0.17	—[e]	—[e]
14	636 (361,000)	645	0.25	—[e]	—[e]
15	636 (343,000)	646	0.16	—[e]	—[e]
16	636 (381,000)	646	0.28	—[e]	—[e]
17	—[d]	—[d]	—[d]	761	0.02
18	—[d]	—[d]	—[d]	761	0.02
19	637 (374,000)	646	0.27	—[e]	—[e]

[a] Measured on 1.0×10^{-6} mol dm^{-3} of substrate at 25 °C.
[b] Measured by absolute PL quantum yield measurement system C9920-02.
[c] λ_{ex}: 630 nm.
[d] Not measured.
[e] Not observed.

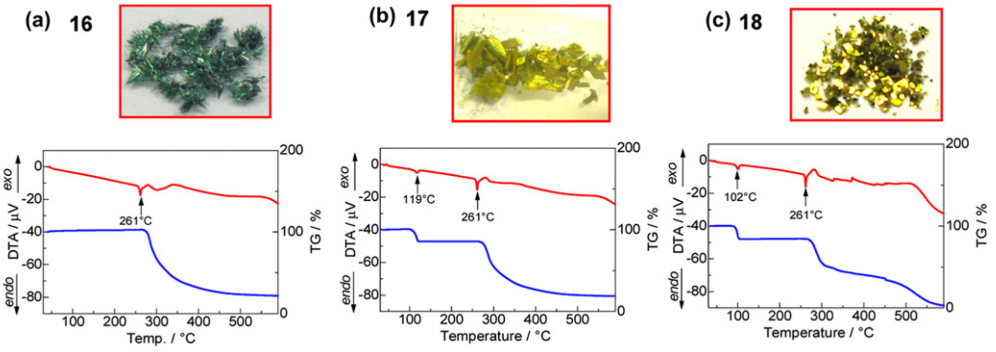

Fig. 1. TG–DTA measurements of (a) **16**, (b) **17**, and (c) **18**.

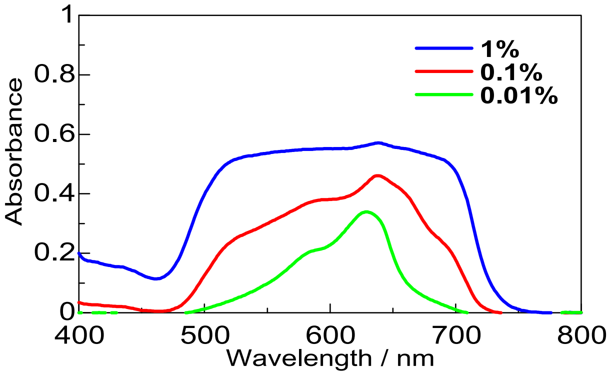

Fig. 3. Reflection spectra (Kubelka-Munk unit) of **16** in potassium bromide.

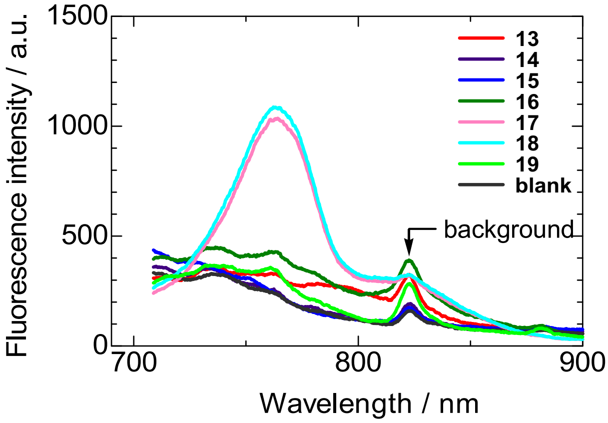

Fig. 4. Solid-state fluorescence spectra of **13**–**19** (λ_{ex}: 630 nm).

The single X-ray crystallography of **16** is shown in Fig. 5. Molecules form a pair of head-to-tail dimer as depicted in over view. The shape of the dimer is like a barrel. A side view (1) indicates that the interplanar distance at the central part of the dimer is longer than that at the terminal ones. π/π-Interactions are observed at both the terminal. Methyl groups could act as steric hindrance for molecules A and B as shown in top view (1) and side view (1). Top view (2) and side view (2) depict that molecules A, C, and D are arranged almost in parallel with six CH/O interactions.

The single X-ray crystallography of **17** is shown in Fig. 6. A toluene molecule is included in the cage of four SQ molecules. The probability of the arranged direction of the toluene molecule is 50%. CH/π-interactions are observed between the toluene and two SQ molecules C and D as shown in side view (2). Toluene and *p*-xylene could fit the size of the cage. The interplanar distance between A and B is 9.29 Å, clearly indicating no interactions between them. The interplanar distance between C and D is 9.99 Å, also showing no interactions between them. There are eight CH/O short contacts among A, E, and F, forming network planar arrangement as shown in top view (3) and side view (3). These interactions could quench the solid-state fluorescence as in the case of **16**. However, as the included toluene could inhibit π/π-intermolecular interactions between A and B, as well as C and D, compounds **17** could exhibit fluorescence in the solid state.

We suppose that the clathrate crystals are formed by the balance of intermolecular interactions between the SQ substrate and guest molecule. When the alkyl group is short, the π/π interactions between the SQ substrates are predominant due to the large π-plane. When the alkyl group is long, both the π/π and alkyl–alkyl

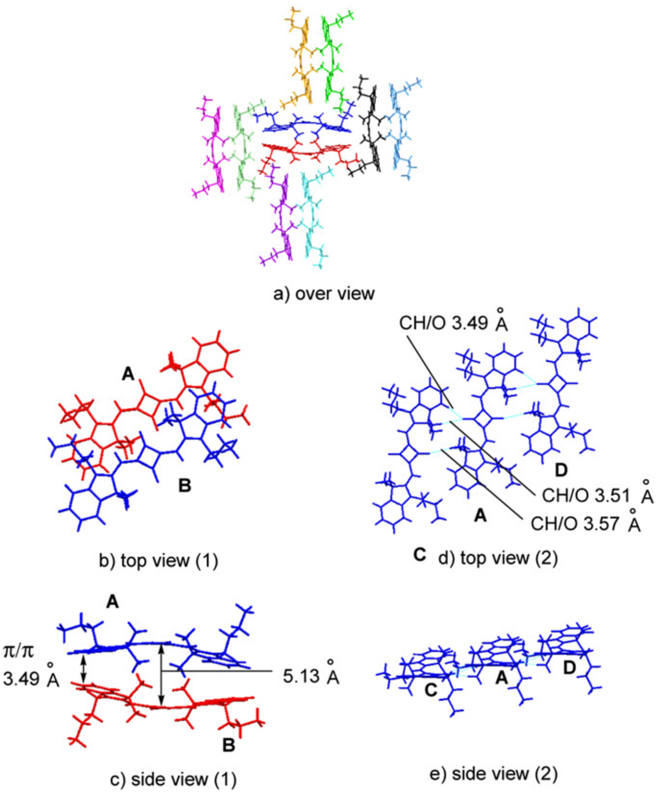

Fig. 5. Single X-ray crystallography of **16**.

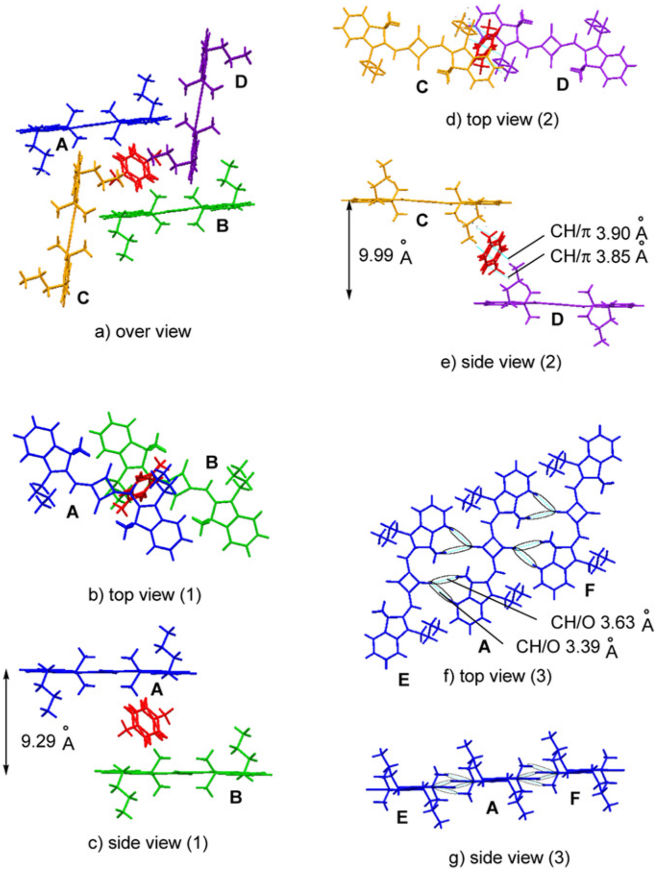

Fig. 6. Single X-ray crystallography of **17**.

interactions may be important to decide the crystalline form. When the alkyl group is medium such as butyl, suitable interactions between the SQ substrate and guest molecule could form the thermodynamically stable clathrate crystals. The size of toluene and *p*-xylene, which fit the cage formed by the SQ substrate could be also an important factor to form the clathrate crystal.

3. Conclusion

We have serendipitously found that only an *N*-butyl indolenine SQ derivative could include toluene and *p*-xylene. These clathrate crystals exhibited solid-state fluorescence at 761 nm with Φ_f 0.02 whereas the non-enclathrated derivatives were non-fluorescent. The X-ray crystallography suggests that the enclathrated guest molecule could prevent π/π-interactions between the SQ fluorophores to exhibit solid-state fluorescence.

4. Experimental section

4.1. General

Melting points were measured with a Yanaco MP-13 micromelting-point apparatus. NMR spectra were obtained by a JEOL JNM-ECX 400P spectrometer. Mass spectra were taken on a JEOL MStation 700 spectrometer. UV–vis absorption and fluorescence spectra were taken on Hitachi U-3500, U-4000, and F-4500 spectrophotometers, respectively. Thermal and elemental analyses were performed on SII technology TG/DTA6300 and Yanako CHN coda MT-6, respectively. Compounds **1**, **3**, **4**, **5**, **6**, and **12** were purchased from TOKYO CHEMICAL INDUSTRY CO., LTD. Compound **2** was obtained from NACALAI TESQUE, INC. 1-Alkyl-2,3,3-trimethyl-3*H*-indolenium iodides **7**,[20] **8**,[21] **9**,[22] **10**,[20] and **11**[23] were prepared as described in the literature.

4.2. Synthesis of SQ dyes 13–16 and 19

To a butanol/benzene (4:1) mixed solution (30 ml) were added 1-alkyl-2,,3,3-trimethyl-3*H*-indolenium iodide (3.30 mmol), 3,4-dihydroxy-3-cyclobuten-1,2-dione (170 mg, 1.50 mmol), and quinoline (2 ml). The mixture was refluxed for 1–2 days. After the reaction was completed, the solvent was removed in vacuo. The resulting precipitate was washed with hexane, purified by column chromatography (SiO_2, **13**: AcOEt, **14**, **15**, **16**, **19**: AcOEt/$CHCl_3$=1:1), and recrystallized from ethanol. The physical and spectral data are shown below.

*4.2.1. SQ dye **13**[24].* Yield 24%; mp 302–303 °C; IR (KBr) ν 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.78 (s, 12H), 3.56 (s, 6H), 5.92 (s, 2H), 7.01 (d, *J*=7.4 Hz, 2H), 7.15 (t, *J*=7.4 Hz, 2H), 7.31 (t, *J*=7.4 Hz, 2H), 7.35 (d, *J*=7.4 Hz, 2H); FABMS (NBA) *m*/*z* 425 (MH^{+}). Anal. Found: C, 79.07; H, 6.83; N, 6.48%. Calcd for $C_{28}H_{28}N_2O_2$: C, 79.22; H, 6.65; N, 6.60%.

*4.2.2. SQ dye **14**.* Yield 54%; mp 284–285 °C; IR (KBr) ν 1592 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.04 (t, *J*=7.3 Hz, 6H), 1.79 (s, 12H), 1.86 (sex, *J*=7.3 Hz, 4H), 3.83–4.10 (m, 4H), 5.96 (s, 2H), 6.99 (d, *J*=7.4 Hz, 2H), 7.14 (t, *J*=7.4 Hz, 2H), 7.30 (t, *J*=7.4 Hz, 2H), 7.36 (d, *J*=7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=11.5, 20.5, 27.2, 45.2, 49.4, 86.7, 109.5, 122.3, 123.7, 127.8, 142.3, 142.6, 170.2, 179.6, 182.5; FABMS (NBA) *m*/*z* 481 (MH^{+}). Anal. Found: C, 79.95; H, 7.55; N, 5.82%. Calcd for $C_{32}H_{36}N_2O_2$: C, 79.96; H, 7.55; N, 5.83%.

*4.2.3. SQ dye **15**.* Yield 39%; mp 288–290 °C (282 °C[25]); IR (KBr) ν 1597 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.63 (d, *J*=6.9 Hz, 12H), 1.73 (s, 12H), 4.95 (br s, 2H), 6.05 (s, 2H), 7.13 (t, *J*=7.4 Hz, 2H), 7.21 (d, *J*=7.4 Hz, 2H), 7.27 (t, *J*=7.4 Hz, 2H), 7.36 (d, *J*=7.4 Hz, 2H); FABMS (NBA) *m*/*z* 481 (MH^{+}). Anal. Found: C, 79.74; H, 7.73; N, 5.74%. Calcd for $C_{32}H_{36}N_2O_2$: C, 79.96; H, 7.55; N, 5.83%.

*4.2.4. SQ dye **16**.* Yield 39%; mp 261–262 °C; IR (KBr) ν 1593 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.98 (t, *J*=7.3 Hz, 6H), 1.43 (sex, *J*=7.3 Hz, 4H), 1.70–1.85 (m, 16H), 3.98 (br s, 4H), 5.95 (s, 2H), 6.97 (d, *J*=7.4 Hz, 2H), 7.12 (t, *J*=7.4 Hz, 2H), 7.29 (t, *J*=7.4 Hz, 2H), 7.34 (d, *J*=7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.8, 20.4, 27.0, 29.1, 43.5, 49.2, 86.5, 109.3, 122.3, 123.6, 127.7, 142.2, 142.5, 170.0, 179.4, 182.4; FABMS (NBA) *m*/*z* 509 (MH^{+}). Anal. Found: C, 80.33; H, 8.18; N, 5.46%. Calcd for $C_{34}H_{40}N_2O_2$: C, 80.28; H, 7.93; N, 5.51%.

*4.2.5. SQ dye **19**.* Yield 20%; mp 204–205 °C; IR (KBr) ν 1599 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, *J*=7.4 Hz, 6H), 1.20–1.49 (m, 20H), 1.75–1.88 (m, 16H), 3.97 (br s, 4H), 5.96 (s, 2H), 6.97 (d, *J*=7.8 Hz, 2H), 7.14 (t, *J*=7.8 Hz, 2H), 7.31 (t, *J*=7.8 Hz, 2H), 7.35 (d, *J*=7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=14.1, 22.6, 27.0, 27.1, 29.1, 29.3, 31.7, 43.7, 49.2, 86.5, 109.3, 122.2, 123.6, 127.7, 142.2, 143.4, 169.9, 179.5, 182.3; FABMS (NBA) *m*/*z* 621 (MH^{+}). Anal. Found: C, 81.34; H, 8.96; N, 4.35%. Calcd for $C_{42}H_{56}N_2O_2$: C, 81.24; H, 9.09; N, 4.51%.

4.3. Clathrate crystals 17 and 18

SQ dye **16** was recrystallized from toluene and *p*-xylene to give **17** and **18**, respectively.

*4.3.1. Clathrate crystal **17**.* IR (KBr) ν 1593 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.99 (t, *J*=7.3 Hz, 6H), 1.44 (sex, *J*=7.3 Hz, 4H), 1.70–1.85 (m, 16H), 2.34 (s, 3H), 3.99 (br s, 4H), 5.96 (s, 2H), 6.97 (d, *J*=7.4 Hz, 2H), 7.13 (t, *J*=7.4 Hz, 2H), 7.15–7.18 (m, 3H), 7.22–7.31 (m, 4H), 7.29 (t, *J*=7.4 Hz, 2H), 7.34 (d, *J*=7.4 Hz, 2H). Anal. Found: C, 81.92; H, 8.19; N, 4.83%. Calcd for $C_{41}H_{48}N_2O_2$: C, 81.96; H, 8.05; N, 4.66%.

*4.3.2. Clathrate crystal **18**.* IR (KBr) ν 1593 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.98 (t, *J*=7.3 Hz, 6H), 1.44 (sex, *J*=7.3 Hz, 4H), 1.70–1.85 (m, 16H), 2.35 (s, 6H), 3.99 (br s, 4H), 5.96 (s, 2H), 6.98 (d, *J*=7.4 Hz, 2H), 7.06 (s, 4H), 7.13 (t, *J*=7.4 Hz, 2H), 7.29 (t, *J*=7.4 Hz, 2H), 7.35 (d, *J*=7.4 Hz, 2H). Anal. Found: C, 82.24; H, 8.48; N, 4.64%. Calcd for $C_{42}H_{50}N_2O_2$: C, 82.04; H, 8.20; N, 4.56%.

4.4. Single X-ray crystallography of 16 and 17

The diffraction data of **16** and **17** were collected by Rigaku R-AXIS RAPID (Cu Kα, λ=1.54187 Å) and AFC-7R (Mo Kα, λ=0.71069 Å) Mercury CCD diffractometers, respectively. The structure was solved by direct methods and refined by fill-matrix least-squares calculations. Crystal data for **16**: $C_{34}H_{40}N_2O_2$, Mw=508.70, monoclinic, *P*21/*c*, *Z*=4, *a*=9.1983(2), *b*=19.9808(4), *c*=15.400(1) Å, β=98.279(7)°, D_{calcd}=1.206 g cm^{-3}, *T*=153 K, 64,687 reflections were collected, 5061 unique (R_{int}=0.0408), 349 parameters, R_1=0.0430, wR_2=0.1105, G.O.F 1.058, CCDC (828353). Crystal data for **17**: $C_{34}H_{40}N_2O_2$ C_7H_8, Mw=600.81, monoclinic, *P*21/*n*, *Z*=2, *a*=9.1717(12), *b*=11.1215(15), *c*=16.869(2) Å, β=101.952(10)°, D_{calcd}=1.185 g cm^{-3}, *T*=123 K, 4559 reflections were collected, 3333 unique (R_{int}=0.0555), 277 parameters, R_1=0.0611, wR_2=0.1797, G.O.F 0.764, CCDC (828354).

Supplementary data

^{1}H NMR spectra of **16**, **17**, and **18**, picture and solid-state fluorescence spectra of **17** before and after heating, and X-ray crystallographic data of **16** and **17**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.12.067. These data include MOL files and InChIKeys of the most important compounds described in this article.

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