Tetrahedron 69 (2013) 3410–3414

Contents lists available at SciVerse ScienceDirect

Tetrahedron

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

Solid-state fluorescence of 6-aryl-9-(dibutylamino)benzo[*a*]phenoxazin-5-ones

Masaki Matsui *, Yukiyo Ando, Osamu Tokura, Yasuhiro Kubota, Kazumasa Funabiki

Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

A R T I C L E I N F O

Article history:
Received 15 January 2013
Received in revised form 18 February 2013
Accepted 22 February 2013
Available online 26 February 2013

Keywords:
Solid state
Naphthooxazine dyes
Single X-ray crystallography
Fluorescence
Near-infrared solid-state fluorescence

A B S T R A C T

6-(9-Anthryl)- and 6-(1-naphthyl)-9-(dibutylamino)benzo[*a*]phenoxazin-5-ones exhibited fluorescence maximum at around 700 nm in the crystalline form. Their fluorescence quantum yields were significantly higher than that of previously reported 6-perfluoro[4-methyl-3-(1-methylethyl)pent-2-en-2-oxy] derivative due to the isolated dimer-type packing.

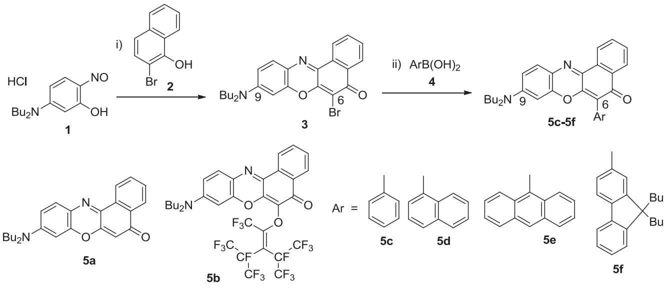
1. Introduction

Survey of solid-state fluorescent organic compounds is one of the most exciting subjects in connection with emitters in organic electroluminescence (EL) device,[1] solid-state dye laser,[2] and probes.[3] Especially, as near-infrared fluorescence can improve photon penetration through tissue, organic fluorophores have been used as in vivo imaging materials.[4] As fluorescence intensity in the solid state is usually reduced due to the wide aromatic moiety of the fluorophores, the introduction of bulky substituent(s) into the fluorophores can inhibit the π/π-interactions to improve the intensity. Nile Red, used as a hydrophobic probe[5] and a pH sensor,[6] is a strongly fluorescent compound in solution and has a wide π-electron system. Recently, Nile Red derivatives have been proposed as red emitters in EL devices.[7] In our previous paper, 9-dibutylamino-6-perfluoro[4-methyl-3-(1-methylethyl)pent-2-en-2-oxy]benzo[*a*]phenoxazin-5-one has been reported to show the fluorescence maximum ($F_{\max}$) at 717 nm with a fluorescence quantum yield (Φ_f) 0.02 in a powder form.[8] As there are few neutral compounds, which exhibit $F_{\max}$ beyond 700 nm in the solid state, 9-(dialkylamino)benzo[*a*]phenoxazin-5-ones are interesting fluorophores. We considered that the Φ_f of this derivative in the solid state is low compared to that in solution due to 24 CH/F and π/π-interactions. Therefore, when a bulky aryl group is introduced into the fluorophore, the solid-state fluorescence quantum yield could be improved. We report herein the effect of an aryl group at the 6-position on the solid-state florescence intensity of 9-(dibutylamino)benzo[*a*]phenoxazin-5-ones.

2. Results and discussion

2.1. Synthesis

Nile Red-Bu (**5a**) and 6-perfluoro[4-methyl-3-(1-methylethyl)pent-2-en-2-oxy] derivative **5b** were prepared as described in our previous paper.[7] 6-Aryl-9-(dibutylamino)benzo[*a*]phenoxazin-5-ones **5c**–**5f** were prepared as shown in Scheme 1. 5-Dibutylamino-2-nitrosophenol hydrochloride salt (**1**) was allowed to react with 2-bromo-1-naphthol (**2**) to give 6-bromo-9-(dibutylamino)benzo[*a*]



Scheme 1. Reagents and conditions: (i) **1** (10 mmol), **2** (10 mmol), DMF (60 mL), reflux, 4 h; (ii) **3** (1.0 mmol), **4** (2.0 mmol), $Pd_2(dba)_3$ (4 mol %), SPhos (8 mol %), aq 2 M Na_2CO_3 (10 mL, 20 mmol), EtOH/toluene (1/4) (26 mL), 100 °C, 15 h.

---

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

0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.02.083

phenoxazin-5-one (**3**), followed by the reaction with arylboronic acids **4c**–**4f** to give **5c**–**5f**.

2.2. UV–vis absorption and fluorescence spectra

Fig. S1 in Supplementary data depicts the UV–vis absorption and fluorescence spectra of **5e** in various solvents. Compound **5e** exhibited the most intense fluorescence in dichloromethane. Therefore, those of the other derivatives were measured in dichloromethane. Fig. 1 shows the UV–vis absorption and fluorescence spectra of **5a**–**5f** in dichloromethane. The results are also summarized in Table 1. These compounds showed the UV–vis absorption maximum (λ_{max}) in the range of 543–577 nm. The λ_{max} of **5b** was most bathochromic among **5a**–**5f** due to the electron-withdrawing nature of a perfluoroalkenyloxy group at the 6-position. The F_{max} was observed in the range of 609–634 nm, the Stokes shift being 54–83 nm. The Φ_f and fluorescence lifetime (τ_f) values of **5a** (Φ_f: 0.85, τ_f: 4.6), **5b** (0.79, 4.4), **5c** (0.54, 3.5), **5d** (0.69, 4.2) were greater than those of **5e** (0.20, 1.8) and **5f** (0.14, 1.2). This comes from the faster non-radiative rate constants (k_{nr}) of **5e** and **5f** rather than their slow radiative rate constant (k_f) in dichloromethane.

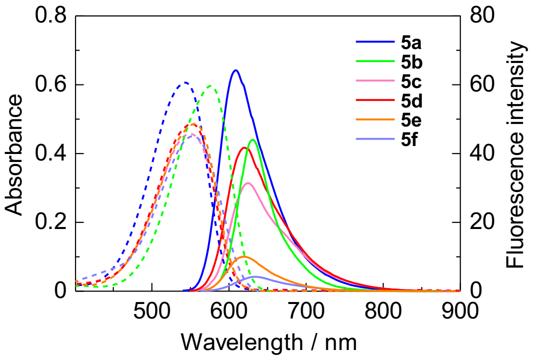


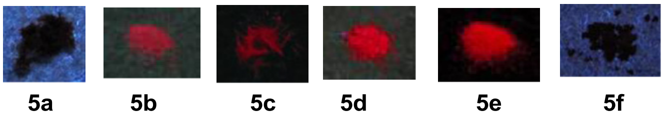
Fig. 1. UV–vis absorption and fluorescence spectra of **5a**–**5f** in dichloromethane. Measured on 1×10^{-5} mol dm^{-3} of substrate at 25 °C.

Table 1
UV–vis absorption and fluorescence spectra of **5a**–**5f**

Compd	In dichloromethane[a]							Solid state		
	λ_{max} (ε)/nm	λ_{ex}/ nm	F_{max}/ nm	Φ_f	τ_f/ ns	k_f[b]/ 10^9 s^{-1}	k_{nr}[c]/ 10^9 s^{-1}	λ_{ex}/ nm	F_{max}/ nm	Φ_f
5a	543 (60,600)	540	609	0.85	4.6	0.19	0.03	—[d]	—[d]	—[d]
5b	577 (59,700)	577	631	0.79	4.4	0.18	0.05	690	732	0.02
5c	549 (45,700)	552	625	0.54	3.5	0.15	0.13	631	686	0.03
5d	552 (48,600)	549	620	0.69	4.2	0.16	0.07	654	711	0.04
5e	555 (48,500)	556	619	0.20	1.8	0.11	0.45	635	694	0.04
5f	551 (38,200)	553	634	0.14	1.2	0.12	0.71	—[d]	—[d]	—[d]

[a] Measured on 1.0×10^{-5} mol dm^{-3} of substrate at 25 °C.
[b] Radiative rate constant ($k_f=\Phi_f/\tau_f$).
[c] Non-radiative rate constant ($k_{nr}=(1-\Phi_f)/\tau_f$).
[d] Too weak to be measured.

The fluorescence spectra of **5a**–**5f** in the crystalline form recrystallized from hexane are indicated in Fig. 2.[9] The results are also listed in Table 1. They showed F_{max} in the range of 686–711 nm. The F_{max} is more bathochromic than that in dichloromethane (609–634 nm) due to the intermolecular interactions in the solid state. Though the Φ_f in the solid state was extremely low compared with those in dichloromethane, the Φ_f in the solid state was significantly more intense in the order of the compounds: **5d** (0.04), **5e** (0.04)>**5c** (0.03), **5b** (0.02)>**5f** (0.00), **5a** (0.00). In the series of solid-state fluorescence of naphthooxazine dyes, compound **5b** has been reported to show the largest Φ_f (0.02) in the powder form with F_{max} at 711 nm.[7] This compound showed Φ_f (0.02) with F_{max} at 732 nm in the crystalline form recrystallized from hexane. Thus, we could find that new compounds **5c**, **5d**, and **5e** exhibit larger Φ_f than known **5b**. The τ_f of **5** was not measured due to low Φ_f in the solid state.



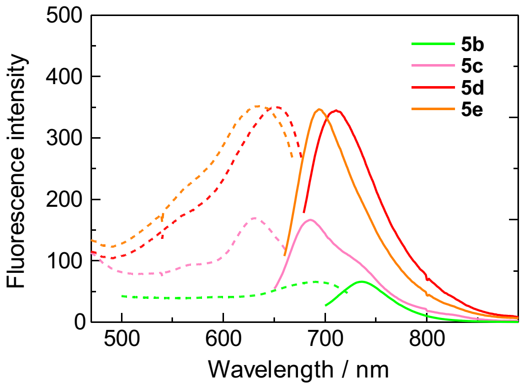


Fig. 2. Solid-state fluorescence spectra of **5c**–**5e**.

2.3. Single X-ray crystallography

To understand why the Φ_f value of these compounds in the solid state changes depending on the substituent at the 6-position, the single X-ray crystallography of **5a**, **5b**, **5c**, **5d**, and **5e** was performed. Fig. 3 shows the single X-ray crystallography of 6-unsubstituted derivative **5a**. Molecules are packed in a herringbone fashion (overview). Molecules A and B are arranged in parallel with π/π-interactions, there being the interplanar distance 3.34 Å (top view and side view). The same results are observed between B and C. Thus, compound **5a** has strong consecutive π/π-interactions.

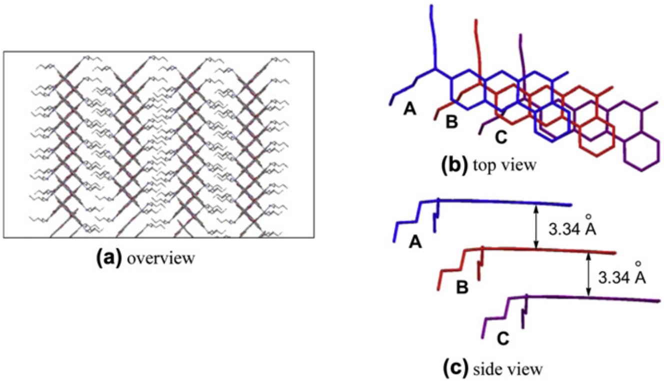


Fig. 3. Single X-ray crystallography of **5a**.

The single X-ray crystallography of **5b** is depicted in Fig. 4. Molecules form a pair of head-to-tail dimers (overview (1)). A molecule has 24 CH/F interactions with adjacent molecules (overview (2)). Molecules A and B are arranged in parallel by π/π-interactions with interplanar distance 3.52 Å (top view (2) and side view (2)). No π/π-interactions are observed between B and C (top view (3)). Molecule B also has small π/π-interactions with D at the edge of naphthooxazine ring (top view (4) and side view (2)). Thus, **5b** has loosely consecutive π/π-stacking and 24 CH/F interactions.

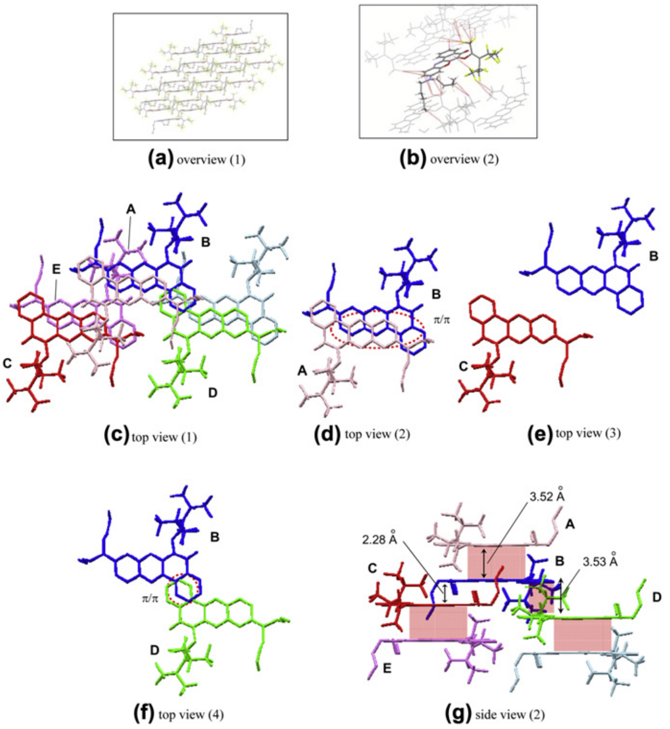


Fig. 4. Single X-ray crystallography of **5b**.

The single X-ray crystallography of **5c** is indicated in Fig. 5. Molecules are packed in a herring-bone fashion (overview). Molecules A and B are arranged in parallel with π/π-interactions, there being the interplanar distance 3.54 Å (top view and side view). The same results are observed between B and C. Thus, compound **5c** has consecutive π/π-interactions (side view). The dihedral angle between the phenyl ring at the 6-position and naphthooxazine fluorophore is 66.9° (side view). Thus, though the phenyl ring is not bulky enough to prevent the π/π-interactions between the naphthooxazine fluorophores, the interplanar distance between A and B in **5c** (3.54 Å) is significantly longer than that in **5a** (3.34 Å).

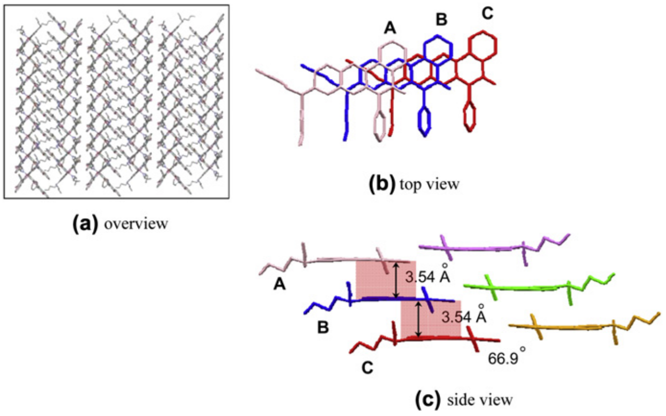


Fig. 5. Single X-ray crystallography of **5c**.

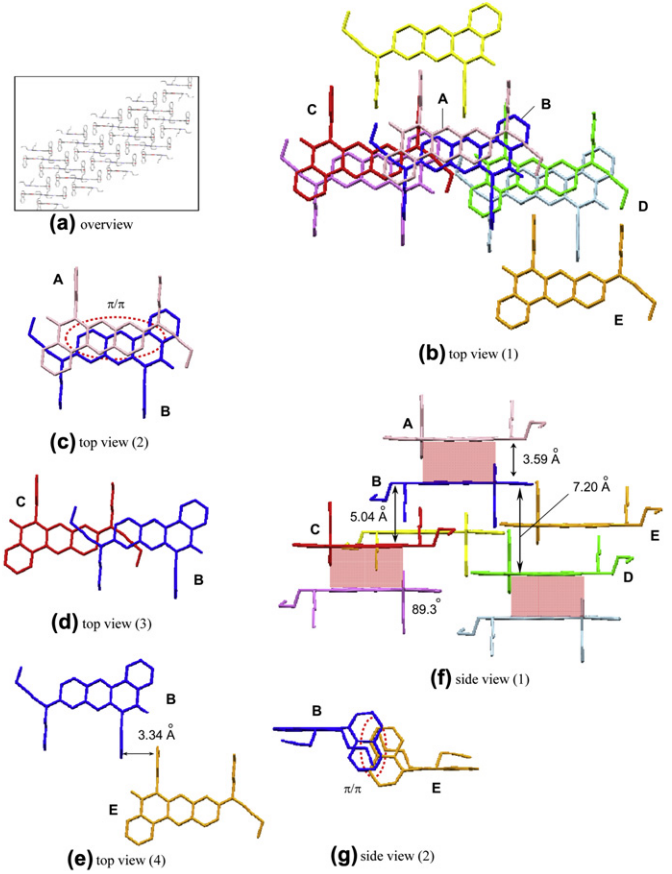


Fig. 6. Single X-ray crystallography of **5d**.

Fig. 6 indicates the single X-ray crystallography of **5d**. Molecules form a pair of head-to-tail dimer and are packed in parallel (overview). Molecule A has π/π-interactions with B, there being the interplanar distance 3.59 Å (top view (2) and side view (1)). The dihedral angle between the naphthyl ring and naphthooxazine fluorophore is 89.3° (side view (1)). Though, for molecule B, the neighboring molecules C and D are also packed in parallel, the interplanar distance is too long to have π/π-interactions, there being, 5.04 and 7.20 Å, respectively (side view (1)). Thus, 1-naphthyl group is sufficiently bulky to inhibit consecutive π/π-stacking. Molecule E is also packed in parallel for B. π/π-interactions are observed between the naphthyl groups (top view (4) and side view (2)). Thus, **5d** has isolated dimer-type packing.

The single X-ray crystallography of **5e** is shown in Fig. 7. Molecules form a pair of head-to-tail dimer and are packed in parallel (overview). Molecule A has π/π-interactions for B with interplanar distance 3.87 Å (top view (2) and side view (1)). This interplanar distance is longer than that of **5d** (3.59 Å). Though molecule C is arranged in parallel for B, no π/π-interactions are observed (top view (3)). The dihedral angle between the anthryl group at the 6-position and naphthooxazine fluorophore is 95.3° (side view (1)). Molecule E is also packed in parallel for B (side view (1)). π/π-Interactions are observed between the anthryl groups with interplanar distance 3.42 Å (top view (4) and side view (2)). Thus, **5e** has isolated dimer-type packing.

Compounds **5a** and **5c** have similar consecutive π/π-stacking. As the intermolecular distance between a pair of dimers in **5c** (3.54 Å) is slightly longer than that of **5a** (3.34 Å), **5c** could exhibit solid-state fluorescence. Compound **5b** has loosely consecutive π/π-stacking and 24 CH/F interactions to exhibit weak fluorescence in the solid state. Compounds **5d** and **5e** have similar isolated dimer-type packing. The $F_{\max}$ of **5e** and **5d** in dichloromethane was observed at 619 and 620 nm, respectively, there being no remarkable differences. Those of **5e** and **5d** in the crystalline form were observed at 694 and 711 nm, respectively. Thus, the $F_{\max}$ of **5e** is significantly hypsochromic compared with **5d**. The Φ_f of **5d** and **5e** in solution is 0.69 and 0.20, respectively. Those in the solid state are 0.04 and 0.04, respectively. Therefore, the reduction ratio of Φ_f of **5e** in the crystalline form (0.04/0.20) is less than that of **5d** (0.04/0.69).

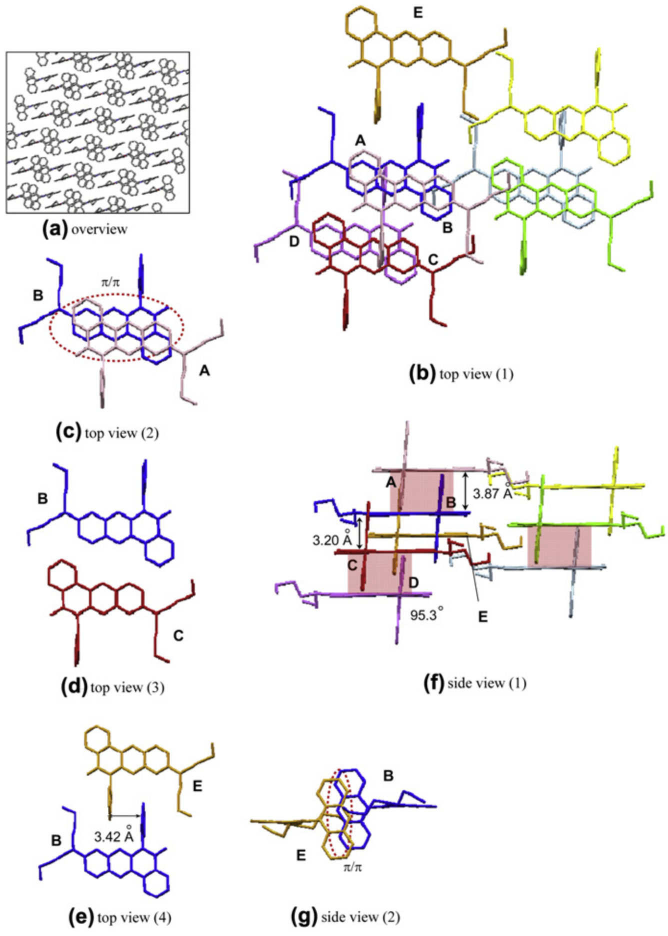


Fig. 7. Single X-ray crystallography of **5e**.

These results could come from longer interplanar distance of **5e** (3.87 Å) than that of **5d** (3.59 Å). Though **5c**, **5d**, and **5e** could show significantly larger Φ_f than previously reported **5b** in the solid state, the Φ_f is still low, there being 0.030.04. As the naphthooxazine ring is a widely planar π-plane, π/π-interactions are easily produced. Even bulky 6-(9-anthryl) derivative **5e** has isolated dimer-type packing. No emission from the eximer was observed. Therefore, to produce more intensely fluorescent naphthooxazine dyes in the solid state, it is essential to make a molecular design to form isolated monomer type packing.

3. Conclusions

9-Dibutylamino-6-(1-naphthyl)- and -6-(9-anthryl)benzo[*a*] phenoxazin-5-ones showed F_{max} at around 700 nm in the crystalline form. The fluorescence of these compounds was more intense than previously reported 6-perfluoro(4-methyl-3-(1-methylethyl) pent-2-en-2-oxy) derivative due to the isolated dimer-type packing.

4. Experimental

4.1. Instruments

Melting points were measured with a Yanaco MP-13 micromelting-point apparatus. NMR spectra were obtained by a JEOL ECX 400P spectrometer. Elemental analysis was performed with a Yanaco MT-6 CHN corder. UV–vis absorption and fluorescence spectra were taken on Hitachi U-4100 and JASCO FP-8600 instruments, respectively. The fluorescence quantum yield and fluorescence lifetime were measured by Hamamatsu Photonics Quataurus-QY and Quantaurus-τ, respectively.

4.2. Materials

3-(Dibutylamino)phenol (**1**), 1-naphthaleneboronic acid (**4d**), 9-anthraceneboronic acid (**4e**), tetrakis(triphenylphpophine), and palladium(0) ($Pd(PPh_3)_4$) were purchased from TOKYO CHEMICAL INDUSTRY CO., LTD. Phenylboronic acid (**4c**) and 2-dicyclohexylphosphyno-2′,6′-dimethoxybiphenyl (SPhos) were obtained from Sigma–Aldrich. Tris(dibenzylidene acetone)diparadium ($Pd_2(dba)_3$) was supplied from KANTO CHEMICAL CO., INC. 2-Bromo-1-naphthol (**2**)[10] and 9,9-dibutylfluoreneboronic pinacol ester (**4f**)[11] were prepared as described in the literature. 9-Dibuthylamino-5*H*-benzo[*a*]phenoxazine-5-one (**5a**) and 9-dibuthylamino-6-perfluoro (4-methyl-3-(1-methylethyl)pent-2-en-2-oxy)-5*H*-benzo[*a*]phenoxazine-5-one (**5b**) were prepared as described in our previous paper.[8]

4.3. Synthesis of 6-bromo-9-dibuthylamino-5*H*-benzo[*a*] phenoxazine-5-one (3)

To a DMF solution (60 mL) of 2-bromo-1-naphthol (**2**, 2.231 g, 10 mmol) was added 5-dibutylamino-2-nitrosophenol hydrochloric acid (**1**, 2.688 g, 10 mmol). The mixture was refluxed for 4 h. After the reaction was completed, the solvent was removed in vacuo. The product was isolated by column chromatography (SiO_2, CH_2Cl_2/AcOEt (v/v=40:1)). Yield 1.36 g (30%); mp 185–187 °C; ^{1}H NMR ($CDCl_3$) δ=1.00 (t, *J*=7.3 Hz, 6H), 1.42 (sex, *J*=7.3 Hz, 4H), 1.66 (quin, *J*=7.3 Hz, 4H), 3.41 (t, *J*=7.3 Hz, 4H), 6.58 (d, *J*=2.7 Hz, 1H), 6.70 (dd, *J*=9.1 and 2.7 Hz, 1H), 7.64 (d, *J*=9.1 Hz, 1H), 7.66 (t, *J*=7.3 Hz, 1H), 7.73 (t, *J*=7.3 Hz, 1H), 8.38 (d, *J*=7.3 Hz, 1H), 8.67 (d, *J*=7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.94, 20.29, 29.42, 51.28, 96.58, 110.56, 112.04, 123.87, 124.72, 126.30, 130.04, 130.82, 130.98, 131.08, 131.59, 138.36, 146.48, 147.58, 151.46, 177.19. Anal. Found: C, 63.55; H, 5.37; N, 6.22%. Calcd for $C_{24}H_{25}BrN_2O_2$: C, 63.58; H, 5.56; N, 6.18%.

4.4. Synthesis of 6-aryl-9-dibutylamino-5*H*-benzo[*a*]phenoxazine-5-ones 5

To ethanol/toluene (1:4) mixed solvent (25 mL) were added 6-bromo-9-dibutylamino-5*H*-benzo[*a*]phenoxazine-5-one (**3**, 453 mg, 1.0 mmol), an arylboronic acid (**4**, 2.0 mmol), tri(dibenzylideneacetone) dipalladium ($Pd_2(dba)_3$, 37 mg, 4 mol %), dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos, 33 mg, 8 mol %), and aqueous 2 M sodium carbonate (10 mL). The mixture was heated at 100 °C for 15 h. After the reaction was completed, the mixture was filtered. The filtrate was poured into water. The product was extracted with ethyl acetate (50 mL×3), dried over anhydrous sodium sulfate, and purified by column chromatography (SiO_2, toluene/ethyl acetate=20:1).

*4.4.1. 9-Dibutylamino-6-phenyl-5H-benzo[a]phenoxazine-5-one (**5c**).* Yield 356 mg (79%); mp 207–208 °C; ^{1}H NMR ($CDCl_3$) δ=0.96 (t, *J*=7.6 Hz, 6H), 1.36 (sex, *J*=7.6 Hz, 4H), 1.59 (quin, *J*=7.6 Hz, 4H), 3.33 (t, *J*=7.6 Hz, 4H), 6.28 (d, *J*=2.7 Hz, 1H), 6.63 (dd, *J*=8.9 and 2.7 Hz, 1H), 7.39 (t, *J*=7.4 Hz, 1H), 7.49 (t, *J*=7.4 Hz, 2H), 7.56 (d, *J*=7.4 Hz, 2H), 7.60 (d, *J*=8.9 Hz, 1H), 7.65 (t, *J*=7.6 Hz, 1H), 7.73 (t, *J*=7.6 Hz, 1H), 8.37 (d, *J*=7.6 Hz, 1H), 8.70 (d, *J*=7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.89 (2C), 20.20 (2C), 29.38 (2C), 51.13 (2C), 96.25, 111.01, 115.43, 119.58, 120.11, 120.63, 123.61, 125.65, 126.31, 129.71, 129.87 (2C), 131.08, 131.59, 132.15 (2C), 138.46, 146.69, 149.18, 151.69, 155.52, 183.53; IR (NaCl) ν 1585 cm^{-1}; EIMS (70 eV) *m*/*z* (rel intensity) 450 (M^+, 64), 403 (100). Anal. Found: C, 79.75; H, 6.85; N, 6.25%. Calcd for $C_{30}H_{30}N_2O_2$: C, 79.97; H, 6.71; N, 6.22%.

*4.4.2. 9-Dibutylamino-6-(1-naphthyl)-5H-benzo[a]phenoxazine-5-one (**5d**).* Yield 425 mg (85%); mp 172–174 °C; ^{1}H NMR ($CDCl_3$)

δ=0.90 (t, J=7.3 Hz, 6H), 1.28 (sex, J=7.3 Hz, 4H), 1.51 (quin, J=7.3 Hz, 4H), 3.24 (t, J=7.3 Hz, 4H), 6.01 (d, J=2.8 Hz, 1H), 6.60 (dd, J=9.2 and 2.8 Hz, 1H), 7.36 (t, J=6.9 Hz, 1H), 7.46 (t, J=6.9 Hz, 1H), 7.52 (d, J=6.9 Hz, 1H), 7.60–7.70 (m, 4H), 7.77 (t, J=7.5 Hz, 1H), 7.94 (t, J=6.9 Hz, 2H), 8.38 (d, J=7.5 Hz, 1H), 8.77 (d, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.85 (2C), 20.13 (2C), 29.29 (2C), 50.91 (2C), 96.59, 109.84, 116.67, 123.61, 124.77, 125.55, 125.58, 125.85, 125.91, 126.32, 128.21, 128.32, 128.70, 129.89, 130.39, 130.76, 131.34, 131.52, 131.96, 132.26, 133.80, 139.42, 146.83, 148.79, 150.97, 182.12; IR (NaCl) ν 1586 cm^{-1}; EIMS (70 eV) m/z (rel intensity) 500 (M$^+$, 100), 457 (51); Anal. Found: C, 81.29; H, 6.57; N, 5.52%. Calcd for $C_{34}H_{32}N_2O_2$: C, 81.57; H, 6.44; N, 5.60%.

*4.4.3. 6-(9-Anthryl)-9-dibutylamino-5H-benzo[a]phenoxazine-5-one (**5e**).* Yield 171 mg (31%); mp 296–298 °C; ^{1}H NMR ($CDCl_3$) δ=0.85 (t, J=7.8 Hz, 6H), 1.24 (sex, J=7.8 Hz, 4H), 1.44 (quin, J=7.8 Hz, 4H), 3.17 (t, J=7.8 Hz, 4H), 5.84 (d, J=2.8 Hz, 1H), 6.59 (dd, J=9.2 and 2.8 Hz, 1H), 7.34 (t, J=7.6 Hz, 2H), 7.45 (t, J=7.6 Hz, 2H), 7.63 (d, J=9.2 Hz, 1H), 7.71 (t, J=7.8 Hz, 1H), 7.80–7.84 (m, 3H), 8.08 (d, J=7.6 Hz, 2H), 8.39 (d, J=7.8 Hz, 1H), 8.58 (s, 1H), 8.85 (d, J=7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.81 (2C), 20.09 (2C), 29.25 (2C), 50.83 (2C), 96.72, 109.91, 114.77, 123.73, 124.87, 125.07 (2C), 125.66 (2C), 126.24 (2C), 126.50, 127.32, 127.63, 128.68 (2C), 130.01, 130.60 (2C), 130.82, 131.49, 131.63, 131.77 (2C), 132.25, 139.31, 147.06, 149.68, 151.01, 182.13; IR (KBr) ν 1585 cm^{-1}; EIMS (70 eV) m/z (rel intensity) 550 (M$^+$, 100), 507 (38), 465 (28). Anal. Found: C, 82.59; H, 6.10; N, 5.01%. Calcd for $C_{38}H_{34}N_2O_2$: C, 82.88; H, 6.22; N, 5.09%.

*4.4.4. 9-Dibutylamino-6-[2-(9,9-dibutylfluorenyl)]-5H-benzo[a]phenoxazine-5-one (**5f**).* Yield 26 mg (4%); mp 151–153 °C; ^{1}H NMR ($CDCl_3$) δ=0.70 (t, J=7.5 Hz, 6H), 0.84–0.96 (m, 10H), 1.11 (quin, J=7.5 Hz, 4H), 1.34 (sex, J=7.5 Hz, 4H), 1.58 (quin, J=7.5 Hz, 4H), 2.01 (t, J=7.5 Hz, 4H), 3.30 (t, J=7.5 Hz, 4H), 6.27 (d, J=2.8 Hz, 1H), 6.64 (dd, J=9.2 and 2.8 Hz, 1H), 7.30–7.39 (m, 3H), 7.56–7.69 (m, 4H), 7.73–7.78 (m, 2H), 7.83 (d, J=8.2 Hz, 1H), 8.40 (d, J=6.9 Hz, 1H), 8.72 (d, J=6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=13.94 (2C), 20.24 (2C), 23.25 (2C), 29.50 (2C), 26.17(2C), 29.70, 39.98 (2C), 50.45 (2C), 54.97 (2C), 96.45, 109.91, 118.25, 119.01, 119.68, 123.03, 123.57, 124.90, 125.46, 126.27, 126.72, 126.85, 129.74, 129.93, 130.58, 130.70 (2C), 131.28, 131.57, 131.75, 140.01, 140.25, 141.16, 146.81, 147.71, 149.95, 151.07, 151.18, 182.12; IR (NaCl) ν 1585 cm^{-1}; FABMS (NBA) m/z 651 (MH$^+$). Anal. Found: C, 82.71; H, 8.03; N, 4.17%. Calcd for $C_{45}H_{50}N_2O_2$: C, 83.04; H, 7.74; N, 4.30%.

4.5. Single X-ray crystallography of 5

The single X-ray crystallography of **5a** and **5b** has been reported in our previous paper (**5a**: CCDC 705404, **5b**: CCDC 704026).[7] Single crystals of **5c**, **5d**, and **5e** were obtained by diffusion method using dichloromethane/hexane mixed solvent. The diffraction data were collected by an XtaLAB mini diffractometer using graphite monochromated Mo Kα radiation (λ=0.71075 Å). The structure was solved by direct methods SIR97 and refined by fill-matrix least-squares calculations. Crystal data for **5c**: $C_{30}H_{30}N_2O_2$, M_W=450.56, monoclinic, $P2_1/c$, Z=4, a=5.529(3), b=19.961(10), c=21.576(11) Å, β=91.390(8)°, D_{calcd}=1.257 g cm^{-3}, T=293(2) K, 18,589 reflections were collected, 5369 unique (R_{int}=0.0546), 309 parameters, R_1=0.1049, wR_2=0.2521, GOF=1.065, refinement on F^2. Crystal data for **5d**: $C_{34}H_{32}N_2O_2$, M_W=500.62, triclinic, P-1, Z=2, a=10.200(15), b=11.266(14), c=13.055(18) Å, α=72.63(5)°, β=89.13(5)°, γ=70.92(3)°, D_{calcd}=1.234 g cm^{-3}, T=293(2) K, 13,939 reflections were collected, 6126 unique (R_{int}=0.0541), 345 parameters, R_1=0.1175, wR_2=0.3051, GOF=0.986, refinement on F^2. Crystal data for **5e**: $C_{38}H_{34}N_2O_2$, M_W=550.67, triclinic, P-1, Z=2, a=9.236(14), b=12.342(19), c=13.037(18) Å, α=86.07(4)°, β=79.81(3)°, γ=88.74(3)°, D_{calcd}=1.253 g cm^{-3}, T=293(2)°K, 15,121 reflections were collected, 6622 unique (R_{int}=0.0986), 381 parameters, R_1=0.0835, wR_2=0.1922, GOF=1.016, refinement on F^2.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre (**5c**: CCDC895518, **5d**: CCDC895516, and **5e**: CCDC895517).

Supplementary data

These date include single X-ray crystallographic data for **5c**, **5d**, and **5e**. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tet.2013.02.083.

References and notes

1. (a) Peng, X. *Chem. Mater.* **2011**, *23*, 621–630; (b) Liu, Y.; Tao, X.; Wang, F.; Dang, X.; Zou, D.; Ren, Y.; Jiang, M. *J. Phys. Chem. C* **2008**, *112*, 3975–3981; (c) Chan, C. Y. K.; Zhao, Z.; Lam, J. W. Y.; Liu, J.; Chen, S.; Lu, P.; Mahtab, F.; Chen, X.; Sung, H. H. Y.; Kwok, H. S.; Ma, Y.; Williams, I. D.; Wong, K. S.; Tang, B. Z. *Adv. Funct. Mater.* **2012**, *22*, 378–389.
2. Garcia-Moreno, I.; Costela, A.; Martin, V.; Pintado-Sierra, M.; Sastre, R. *Adv. Funct. Mater.* **2009**, *19*, 2547–2552.
3. For example, Haugland, R. *Handbook of Fluorescent Probes and Research Chemicals*, 8th ed.; Molecular Probes: Eugene, OR, 2001.
4. (a) Pu, K.-Y.; Li, K.; Liu, B. *Adv. Funct. Mater.* **2010**, *20*, 2770–2777; (b) Li, C.; Xia, J.; Wei, X.; Yan, H.; Si, Z.; Ju, S. *Adv. Funct. Mater.* **2010**, *20*, 2222–2230; (c) Hilderbrand, S. A.; Weissleder, R. *Curr. Opin. Chem. Biol.* **2010**, *14*, 71–79; (d) Frangioni, J. V. *Curr. Opin. Chem. Biol.* **2003**, *7*, 626–634.
5. (a) Kucherak, O. A.; Oncul, S.; Darwich, Z.; Yuschenko, D. A.; Arntz, Y.; Didier, P.; Mély, Y.; Klymchenko, A. S. *J. Am. Chem. Soc.* **2010**, *132*, 4907–4916; (b) Lampe, J. N.; Fernandez, C.; Nath, A.; Atkins, W. M. *Biochemistry* **2008**, *47*, 509–516.
6. (a) Peng, H.-S.; Stolwijk, J. A.; Sun, L.-N.; Wegener, J.; Wolfbeis, O. S. *Angew. Chem., Int. Ed.* **2010**, *49*, 4246–4249; (b) Polverini, E.; Cugini, G.; Annoni, F.; Abbruzzetti, S.; Viappiani, C.; Gensch, T. *Biochemistry* **2006**, *45*, 5111–5121.
7. Nakaya, T.; Tajima, A.; Saikawa, T. WO2007046247.
8. Park, S.-Y.; Kubota, Y.; Funabiki, K.; Matsui, M. *Tetrahedron Lett.* **2009**, *50*, 1131–1135.
9. The solid-state fluorescence was measured by a JASCO FP-8600 spectrophotometer. About 3 mg of sample was put on the cell. The solid-state fluorescence was checked by irradiating 500 nm light to obtain F_{max}. On the basis of the measured F_{max}, the exact excitation wavelength (λ_{ex}) was obtained. Finally, the solid-state fluorescence was obtained by irradiating the λ_{ex} light. Both the slit width of excitation and fluorescence sides were 5 nm. The sensitivity was low. To check the reproducibility, the measurement was done four times.
10. Huang, W.-G.; Jiang, Y.-Y.; Li, Q.; Li, J.; Li, J.-Y.; Lu, W.; Cai, J.-C. *Tetrahedron* **2005**, *61*, 1863–1870.
11. Fomiya, M.; Bradforth, S. E.; Hogen-Esch, T. E. *Macromolecules* **2009**, *42*, 6440–6447.