Yellow-green Fluorescence of 5,11- and 5,12-Bis(diisopropylsilyl)naphthacenes

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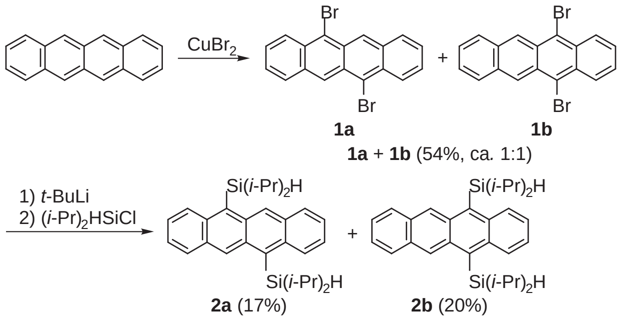
5,11- and 5,12-Bis(diisopropylsilyl)naphthacenes (**2a** and **2b**) were synthesized, and their electronic properties were studied. In UV–visible spectra, the lowest energy absorption bands of **2a** and **2b** are more intense than that of naphthacene. Compounds **2a** and **2b** show intense yellow-green fluorescence, and the fluorescence quantum yields are almost two times higher than that of naphthacene.

Some silyl-substituted aromatic compounds have recently been found to show efficient light emission. For example, we have reported that 9,10-disilylanthracenes show intense fluorescence in high fluorescence quantum yields ($\Phi_f > 0.9$).[1] Watanabe, Matsuda, and a co-worker[2] and Kuriyama and co-workers[3] synthesized polymers in which 9,10-anthrylene groups are connected with polysilane chains and showed that these polymers exhibit intense fluorescence. Mizuno and co-workers have reported that the fluorescence intensity of silyl-substituted pyrenes becomes greater as the number of silyl substituents progressively increases.[4] All of these compounds emit intense blue fluorescence. If silyl substitution on other aromatic compounds induces intense fluorescence with various colors, this methodology would have wide applicability. As part of our studies on organosilicon aromatic compounds,[5] we attempted constructing light-emitting compounds with fluorescence color other than blue. We report herein intense yellow-green fluorescence of disilylnaphthacenes, which are the first examples of silyl-substituted naphthacenes.

5,11- and 5,12-Bis(diisopropylsilyl)naphthacenes were synthesized according to the following equation (Scheme 1). Bromination of naphthacene with copper(II) bromide gave a ca. 1:1 mixture of 5,11- and 5,12-dibromonaphthacenes (**1a** and **1b**). As these isomers could not be easily separated, the mixture was used in the next step without separation. The mixture of **1a** and **1b** was lithiated with *tert*-butyllithium, followed by silylation with chlorodiisopropylsilane to give 5,11- and 5,12-bis(diisopropylsilyl)naphthacenes (**2a** and **2b**) in 17 and 20% yields, respectively.[6] Both isomers could be isolated by recycle-type HPLC.



Scheme 1.

The UV–visible spectra of **2a**, **2b**, and naphthacene are shown in Figure 1. Naphthacene shows the intense ^1B_b band at 273 nm and the ^1L_a band with a vibrational fine structure at the wavelength region of 374–469 nm. The silyl substituents of **2a** and **2b** lead to bathochromic shifts of both bands: the ^1B_b and ^1L_a bands of **2a** are observed at 283 and 383–494 nm, and the ^1B_b and ^1L_a bands of **2b** are observed at 283 and 384–496 nm, respectively. Also, the silyl substituents increase the extinction coefficients of the ^1L_a bands. These results show that the silyl substituents of **2a** and **2b** perturb the π electron system of naphthacene. Since the absorption maxima and extinction coefficients of **2a** and **2b** are quite similar, the effect of the silyl substituents at the 5,11- and 5,12-positions seems almost the same. Molecular orbital calculations at the B3LYP/6-31G* level show that the energy levels of the LUMO's of **2a** (−2.17 eV) and **2b** (−2.20 eV) are lower than that of naphthacene (−2.07 eV) due to the σ^*–π^* conjugation[7] between Si–C(isopropyl) σ^* orbitals and a π^* orbital of naphthacene. The energy levels of the HOMO's of **2a** (−4.85 eV) and **2b** (−4.87 eV) are almost the same as that of naphthacene (−4.86 eV). The smaller energy gaps between the HOMO and the LUMO of **2a** and **2b** than that of naphthacene are in accord with the bathochromic shifts observed in the UV–visible spectra.

Compounds **2a** and **2b** show intense yellow-green fluorescence, while naphthacene shows less intense green fluorescence as shown in Figure 2. In Figure 3, the fluorescence spectra of **2a**, **2b**, and naphthacene are shown. The fluorescence bands of **2a** and **2b** exist in the longer wavelength region with greater intensity than that of naphthacene. The fluorescence quantum yields (Φ_f) of **2a** and **2b** are 0.30 and 0.34, respectively, which are almost two times higher than that of naphthacene (Φ_f 0.17).[8] The higher fluorescence quantum yields of **2a** and **2b** correspond to the more intense ^1L_a bands in Figure 1.

We also measured the fluorescence lifetimes (τ_S) of **2a**, **2b**,

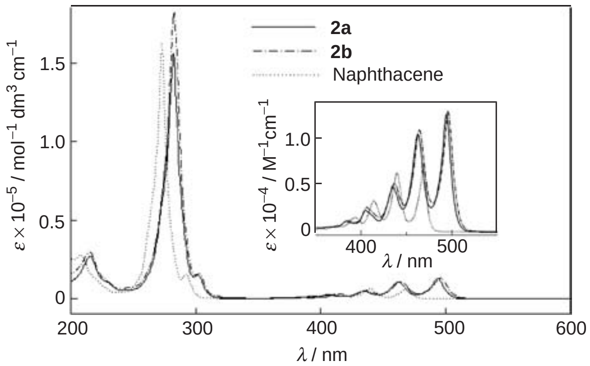


Figure 1. UV–visible spectra of **2a**, **2b**, and naphthacene in hexane at room temperature.

Figure 2. Fluorescence of naphthacene (left), **2a** (middle), and **2b** (right) in hexane at room temperature. The concentrations of the solutions of naphthacene, **2a**, and **2b** are 1.2×10^{-5}, 1.0×10^{-5}, and $1.1 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$, respectively. Excitation was carried out with a low-pressure mercury lamp.

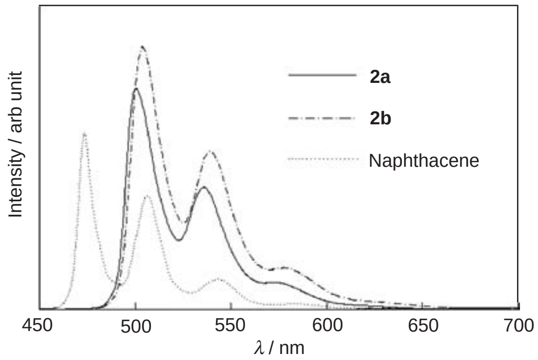


Figure 3. Fluorescence spectra of **2a**, **2b**, and naphthacene in cyclohexane at room temperature.

and naphthacene. By using the Φ_f and τ_S values, fluorescence radiation rate constants (k_f) and the sum of internal conversion rate constants and intersystem crossing rate constants ($k_{ic} + k_{ST}$) were calculated according to Eq 1. The photophysical parameters are summarized in Table 1. The k_f values of **2a** and **2b** are larger than that of naphthacene, and the $k_{ic} + k_{ST}$ values of **2a** and **2b** are smaller than that of naphthacene, indicating that the silyl substituents accelerate the fluorescence radiation process and inhibit the internal conversion and intersystem crossing processes. As a result, the fluorescence quantum yields of **2a** and **2b** become higher than that of naphthacene.

$$\Phi_f = k_f/(k_f + k_{ic} + k_{ST}) = k_f\tau_S. \qquad (1)$$

Table 1. Photophysical parameters of **2a**, **2b**, and naphthacene in cyclohexane at room temperature

Compound	$\lambda^{f}_{0\text{–}0}$/nm	Φ_f	τ_S/ns	k_f/s^{-1}	$k_{ic} + k_{ST}$/s^{-1}
2a	501	0.30	9.52	3.2×10^7	7.4×10^7
2b	504	0.34	10.5	3.2×10^7	6.3×10^7
Naphthacene	473	0.17[a]	6.62	2.6×10^7	1.3×10^8

[a] Ref. 8.

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6 A solution of *tert*-butyllithium in pentane ($1.40\,\mathrm{mol\,dm^{-3}}$, 1.5 mL) was added dropwise to a suspension of a ca. 1:1 mixture of **1a** and **1b** (0.197 g, 0.51 mmol) in diethyl ether (65 mL) at −78 °C. The mixture was allowed to warm gradually to room temperature, and chlorodiisopropylsilane (0.400 g, 2.7 mmol) was added dropwise to the solution. The mixture was stirred at room temperature overnight and hydrolyzed with aqueous sodium hydrogen carbonate. The organic layer was dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was separated by recycle-type HPLC (ODS, methanol–THF (8:2)) to give **2a** (39.5 mg, 17%) as orange crystals and **2b** (46.5 mg, 20%) as orange crystals. **2a**: mp 239–241 °C; ^{1}H NMR (CD_2Cl_2) δ 0.90 (d, 12H, $J = 7.3$ Hz), 1.34 (d, 12H, $J = 7.3$ Hz), 1.78 (sep of d, 4H, $J = 7.3$, 4.9 Hz), 5.03 (t, 2H, $J = 4.9$ Hz), 7.40–7.47 (m, 4H), 8.05 (d, 2H, $J = 8.2$ Hz), 8.56 (d, 2H, $J = 8.6$ Hz), 9.27 (s, 2H); ^{13}C NMR (CD_2Cl_2) δ 13.5, 19.2, 20.0, 124.2, 125.0, 128.1, 129.6, 130.3, 130.6, 132.9, 134.8, 137.2; ^{29}Si NMR (CD_2Cl_2) δ −1.8; IR (KBr) 3070, 2940, 2860, 2130, 1460, 1000, 880, 780, 740 cm^{-1}; UV–visible (λ_{max} (ε) in hexane) 283 (156000), 302 (15200), 383 (1100), 405 (2400), 435 (4900), 463 (10700), 494 nm (13000); MS m/z (%) 456 (M^+, 100), 299 (17), 283 (12), 255 (27), 254 (13), 228 (10); HRMS. Found: 456.2666. Calcd for $C_{30}H_{40}Si_2$: 456.2669. **2b**: mp 113–114 °C; ^{1}H NMR (CD_2Cl_2) δ 0.88 (d, 12H, $J = 7.3$ Hz), 1.34 (d, 12H, $J = 7.3$ Hz), 1.77 (sep of d, 4H, $J = 7.3$, 4.9 Hz), 5.01 (t, 2H, $J = 4.9$ Hz), 7.42 (dd, 2H, $J = 7.1$, 3.3 Hz), 7.43 (dd, 2H, $J = 6.6$, 3.2 Hz), 8.03 (dd, 2H, $J = 6.6$, 3.2 Hz), 8.56 (dd, 2H, $J = 7.1$, 3.3 Hz), 9.21 (s, 2H); ^{13}C NMR (CD_2Cl_2) δ 13.6, 19.2, 20.0, 124.0, 125.0, 127.7, 127.8, 129.6, 130.1, 134.7, 135.7, 137.0; ^{29}Si NMR (CD_2Cl_2) δ −0.5; IR (NaCl) 3050, 2940, 2860, 2130, 1460, 1260, 1010, 880, 800 cm^{-1}; UV–visible (λ_{max} (ε) in hexane) 283 (182000), 302 (16000), 384 (1300), 406 (2700), 436 (5400), 464 (11200), 496 nm (13300); MS m/z (%) 456 (M^+, 100), 299 (15), 297 (17), 283 (19), 257 (10), 255 (12), 228 (11); HRMS. Found: 456.2659. Calcd for $C_{30}H_{40}Si_2$: 456.2669.

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