Synthesis and Characterization of (Di)Benzosilaphenalenes

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Solid-state fluorescent materials were prepared by the annulation of silylated polycyclic aromatic hydrocarbons (PAHs) with internal alkynes catalyzed by [RuH₂(CO)(PPh₃)₃]. Single-crystal X-ray analysis revealed that the annulation proceeded through C–H cleavage at the *peri*-positions and afforded slightly strained six-membered rings containing silicon. In UV–vis absorption and photoluminescence experiments, bathochromic shifts of the annulation product as compared with those of the corresponding substrates were observed.

Keywords: Benzosilaphenalene | Solid-state fluorescent | Polycyclic aromatic hydrocarbon (PAH)

Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are attractive molecules because of their potential application in field-effect transistors¹ and photosensitizers.² Introduction of substituents and expansion of the π -conjugated system are proposed as strategies to tune the aggregation properties, color, emission, and conductivity of PAHs. Siliconcontaining substituents are often used to modify the packing,³ color and fluorescence quantum yields.⁴ For instance, some silvlanthracenes show higher fluorescence quantum yields and red-shifted emission as compared with anthracene.4a Fusion of silicon-containing rings and aromatic hydrocarbon rings has also been found to be effective in perturbing the electronic structure.⁵ Silacyclopentadiene moieties, which show n-type conductivity due to their $\sigma^* - \pi^*$ conjugation, have been condensed to PAHs and their properties investigated in detail. The utility of the silvl groups and silacyclopentadiene moieties have encouraged synthetic chemists to develop direct C-H silylation of PAHs.⁶

In contrast to the five-membered rings containing silicon, the effects of fused six-membered rings containing silicon on the properties of PAH have rarely been investigated probably due to the difficult synthesis. 1-Sila-1H-phenalene is composed of three fused six-membered rings. The conventional synthetic procedures for these compounds require high temperature (ca. 650 °C)⁷ or complex pentacoordinate silicates.⁸ Recently, one of the authors developed a direct and mild synthetic route to 1-sila-1H-phenalene. Ruthenium-catalyzed annulation of hydrosilylnaphthalenes with internal alkynes afforded 1-sila-1H-phenalene in good yield.9 Moreover, the annulation could result in the addition of bulky regions to the substrate. Bulkiness around the chromophore is an important factor to obtain solid-state emission of organic molecules.¹⁰ In this study, we subjected PAHs such as silvlated anthracene, pyrene, and phenanthrene to ruthenium-catalyzed annulation conditions. The use of such large π -conjugated systems would allow for the investigation of absorption and emission properties in the visible region.

Silylated anthracenes, pyrenes, and phenanthrenes were prepared from the brominated precursors via lithium–bromine exchange and subsequent trapping by the chlorosilanes. In the



Scheme 1. Scope of the annulation of silylated PAHs and internal alkynes. Isolated yields are reported. Yields determined by ¹H NMR are reported within parentheses.

presence of [RuH₂(CO)(PPh₃)₃], annulation of the silvlated arenes with alkynes proceeded smoothly at 125 °C through C-H cleavage at the peri-positions (Scheme 1).¹¹ Annulation of 9dimethylsilylanthracene 1a with diphenylacetylene (2a) gave product 3aa in 71% isolated yield and 84% NMR yield. The reactivity of 1a was higher than that of 1-dimethylsilylnaphthalene under conditions similar to those mentioned in the previous report (59% GC yield).9 The high reactivity of 1a could be related to two-fold peri-positions, which increases the probability of activation of an active C-H bond by the ruthenium catalyst. The diethylsilyl group (1b) and diphenylsilyl group (1d) were also tolerated in the annulation. Diisopropylsilvlanthracene (1c), however, was recovered after being subjected to the annulation conditions. Considering 1-diisopropylsilylnaphthalene gave the annulation product in the previous work (44% isolated yield),⁹ it appears that the bulky 9-anthryl group may partially disturb the annulation without affecting the C-H cleavage process. Diphenylacetylenes with isopropoxy groups (2c) and with trifluoromethyl groups (2d) at the parapositions were also effective as the annulation partners of silylanthracene 1. Instead of the silylanthracenes, silylpyrenes



Figure 1. X-ray crystal structures of (a) **3aa**, (b) **3ea**, and (c) **3ga**. Thermal ellipsoids are set to 50% probability level. Hydrogen atoms are omitted for clarity. HOMA values of the individual rings are reported below the crystal structures. As two sets of molecules were contained in the crystal of **3ga**, an averaged HOMA value of **3ga** is reported here.

(1e and 1f) and a silylphenanthrene (1g) were also used as silylated substrates to afford 3ea, 3fb, and 3ga. The yields were lower than those obtained with silylanthracenes but similar to those obtained with silylanphthalenes. Comparison of the annulation results from the silylated hydrocarbons suggested that the 9-anthryl group with two *peri*-positions was suitable for this reaction. The efficiency of C–H cleavage at the *peri*-position may influence the yields of the annulation products.

The structures of 3aa, 3ea, and 3ga were revealed by singlecrystal X-ray analysis (Figure 1).¹² As expected, the rutheniumcatalyzed annulation gave the six-membered rings containing silicon. The fused ring systems were almost planar. As a result of annulation, the bond lengths of the additional moieties by annulation fell within the typical C-C, C=C, and C-Si range, indicating weak π -delocalization effects through the moiety. The interior C-C-C (or Si) angles of the silicon-containing rings were larger than 120° and the C-Si-C angles were smaller than 109°. The deviation from the ideal angles for $C(sp^2)$ and $Si(sp^3)$ suggested some strain in the silicon-containing rings. In order to evaluate the aromaticity of the carbon rings from substrates 1, HOMA indexes were calculated using the bond lengths.¹³ While the HOMA values of rings far from the silicon-containing rings were similar to those of the parent polycyclic aromatic hydrocarbons, such as anthracene, pyrene, and phenanthrene,¹⁴ rings directly fused to the silicon-containing ring tended to show small HOMA values. The decrease in the HOMA values implied that the strain in the silicon-containing rings affected the structures of the adjacent rings.

The UV-vis and photoluminescence properties of the obtained compounds in CHCl₃ were investigated to elucidate the effect of π -extension from 1 to 3 (Table 1). The bath-ochromic shift of the absorption peaks from 1a to 3aa implied effective π -conjugation between the parent anthracene moiety and the silicon-containing ring (Figure 2). A vibronic structure was observed in the absorption band around 400 nm for 3aa. The structure resembled that of 1a, indicating that the anthracene core mainly contributed to the absorption of 3aa. Similar bathochromic shifts and vibronic behavior were observed in UV-vis absorption spectra of the other annulation products

Table 1. Photophysical properties of 1 and 3

Compd.	$\lambda_{\rm abs}/{\rm nm^{a,b}}~(\varepsilon)^{\rm c}$	$\lambda_{\rm em, chloroform}/{\rm nm^{a,d}}~(\varPhi_{\rm F})^{\rm e}$	$\lambda_{ m em,powder}/ m nm^d~(arPsi_F)^e$
1a	390 (770)	396, 419 (0.50)	427, 447 (0.46)
1d	393 (970)	401, 423 (0.66)	429, 448 (0.29)
1e	348 (4720)	378, 396 (0.08)	493 (0.30)
1f	351 (4370)	379, 397 (0.11)	467 (0.22)
1g	301 (1220)	352, 368 (0.10)	369 (0.06)
3aa	419 (1280)	434, 455 (0.36)	455, 482 (0.29)
3db	423 (1010)	435, 459 (0.20)	466, 494 (0.20)
3ac	418 (1250)	496 (0.16)	521 (0.36)
3ad	419 (1290)	431, 455 (0.42)	453, 482 (0.22)
3ea	370 (3810)	395, 454 (0.04)	418, 484 (0.26)
3fb	372 (3820)	391, 412 (0.13)	436 (0.14)
3ga	338 (1650)	377, 433 (0.02)	419 (0.37)

 $^{a}10\,\mu$ M in chloroform. b Observed absorption maximum at the longest wavelength. c Molar extinction coefficient (M⁻¹ cm⁻¹). d Observed fluorescent maxima. e Fluorescent quantum yield determined by a calibrated integrating sphere system.



Figure 2. UV-vis absorption (solid line) and photoluminescence (dotted line) spectra of 1a in chloroform (blue), 3aa in chloroform (red), and 3aa in powder state (green).

regardless of the parent rings and substituents (Figures S1–S5). In particular, substituents on the additional ring fused to the anthracene core hardly affected the absorption properties. Photoluminescence peaks of **3aa** were observed at 434 and 455 nm. The luminescence peak shift from **1a** to **3aa** was similar to the absorption peak shifts, although the Stokes shift of **3aa** was slightly larger than that of **1a**. The vibronic structure in the luminescence spectra of **3aa** suggested that the fused ring system was rigid even in the excited state. The photoluminescence spectra obtained for **3db** and **3ad** were almost the same as that obtained for **3aa** and the trend coincided with their absorption spectra. It is noteworthy that the (4-isopropoxy)phenyl-substituted product (**3ac**) showed red-shifted and broadened photo-luminescence spectra.

Solid-state photoluminescence data of 1 and 3 were also collected (Figures 2 and S1–S6). The silylanthracenes and their annulation products in solid state showed 20–35 nm bathochromic shift as compared with those in solution state and a similar vibronic structure. Moreover, moderate fluorescence quantum yields of 1a, 1d, 3aa, 3db, and 3ad were obtained in the solid state and the yield of 3ac almost doubled upon solidification. These luminescence properties indicated that the silyl groups and additional rings effectively restrained π - π stacking of the anthracene cores leading to broadened peaks and quenching. Aggregation-induced emission enhancement (AIEE) behavior

was observed for the phenanthrene-based compounds. The fluorescence quantum yield of **3ga** in the solid state ($\Phi_{\rm F} = 0.37$) was 18 times higher than that in the solution state ($\Phi_{\rm F} = 0.02$), although the parent silvlphenanthrene (1g) showed low fluorescence quantum yield in both the solution ($\Phi_{\rm F} = 0.10$) and solid states ($\Phi_{\rm F} = 0.06$). Fluorescence peaks of silvlpyrenes (1e and 1f) in the solid state largely shifted to longer wavelengths as compared with those in the solution state. The large bathochromic shift indicated π - π stacking of **1e** and **1f** in the solid state. In contrast, bathochromic shifts of 3ea and 3fb upon solidification were as small as those of the other annulation compounds, which implied that bulky groups installed by the annulation effectively suppressed the π - π stacking of pyrenes (Figures S2 and S3). The packing structures of 3aa, 3ea, and 3ga obtained by single-crystal X-ray analysis might support the emission behavior in the solid state. There was no π - π stacking but many CH– π interactions in the crystals.

The contribution from the additional silicon-containing ring to the UV-vis absorption properties was also investigated by the TD-DFT calculation at the ωB97X-D/def2-SVPD level.¹⁵ The calculated structures were optimized at the $\omega B97X-D/$ def2-SV(P) level, and the fused core structures were in good agreement with the crystal structures. The TD-DFT calculation revealed that absorption at the longest wavelengths in 1a, 3aa, 3ea, and 3ga corresponded to the HOMO-LUMO transitions. The calculated peaks of 1a and 3aa were 329 and 347 nm, respectively. Although the calculated wavelengths were shorter than those obtained from UV-vis absorption experiments, the red-shift of 3aa as compared with 1a was qualitatively reproduced by calculation. The red-shift might be explained by π -delocalization (Figure 3). The HOMO and LUMO of **3aa** were extended from the anthracene moiety to the two additional carbon atoms. A similar delocalization was also seen in 3ea and 3ga (Figure S7). Although little contribution of silicon to the frontier orbitals of 3aa and 3ea was observed, the LUMO of 3ga was extended to the silicon atom, probably due to the close



Figure 3. HOMO and LUMO lobes of (a) 1a and (b) 3aa calculated at ω B97X-D/def2-SVPD// ω B97X-D/def2-SV(P) level.

energy levels between the π^* orbitals of the hydrocarbon moiety and the σ^* orbital of the silicon atom.

In conclusion, ruthenium-catalyzed annulation of silylated anthracene, pyrene, and phenanthrenes with internal alkynes proceeded smoothly through the C–H cleavage at the *peri*position. Single-crystal X-ray analysis revealed that the sixmembered rings containing silicon in the products had slight strain and tended to reduce the aromatic character of the adjacent hydrocarbon rings. Ring fusion induced about 30-nm bathochromic shift in the absorption and emission spectra, except for **3ac**, which showed a larger bathochromic shift (77 nm as compared with **1a**) and broadening in the photoluminescence spectra. Moderate fluorescence quantum yields were obtained even in the solid state of the annulation products probably due to difficult π – π stacking.

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- 11 By using [RuH₂(CO){P(p-FC₆H₄)₃}₃] instead of [RuH₂(CO)-

(PPh₃)₃], **3aa**, **3ea**, and **3ga** were produced in 99%, 50%, and 46% NMR yield, respectively.

- 12 CCDC 1563436 (**3aa**), 1563437 (**3ea**), and 1563438 (**3ga**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
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