Photoluminescence Enhancement in Tetrakis(arylethynyl)silanes

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(Received September 4, 2006; CL-061013; E-mail: orita@high.ous.ac.jp)

Substitution on silicon with arylethynyl groups enhanced photoluminescence in solution to result in high quantum yields of tetrakis(arylethynyl)silanes.

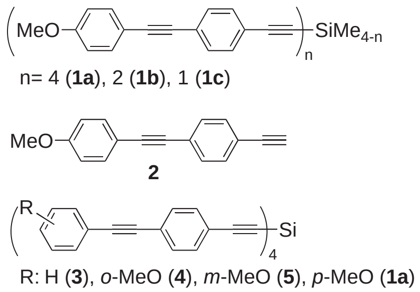
Silyl compounds have attracted extensive attention as photoluminescent materials for electroluminescence (EL) devices[1] since they are not only readily prepared and stable but also exhibit characteristic optical properties. Siloles (silacyclopentadienes) have a narrow HOMO–LUMO band gap because the LUMO level is lowered by σ^*–π^* interaction between C–Si and olefinic bonds to induce strong luminescence.[1] It is known that introduction of silyl groups on planar chromophores such as pyrene,[2] anthracene,[3] and triphenylene[4] enhances fluorescence emission. Recently, Mizuno, Fujimoto, and co-workers revealed that a silylethynyl group enhanced emission as well.[5] In this context, we are intrigued by photoluminescence of tetraethynylsilanes (TETS) to see the electronic effect of the tetrahedral arrangement of ethynylene π orbitals about silicon. We describe herein effects of structural features of arylethynylsilanes on wavelengths and intensities of the emission in solution.

First, emission spectra of arylethynylsilanes **1a**–**1c** and terminal acetylene **2** were recorded in CH_2Cl_2 solution (9.4×10^{-7} M) at rt (Figure 1).[6] Figure 1 indicates that increment of ethynylenes on the silicon atom induces bathochromic shifts of emission λ_{max}. The number of ethynylenes on the silicon atom plays a pivotal role for the intensity and quantum yield of emission, and tetraethynylsilane **1a** exhibits the strongest emission. The relevant emission properties such as quantum yields and life times are summarized in Table 1. Rate constants for radiation (k_r) and radiationless process (k_{nr}) were calculated from equations 1 and 2 on the basis of corresponding quantum yield Φ_F and life time τ.

$$k_r = \Phi_F/\tau. \qquad (1)$$

$$k_{nr} = (1 - \Phi_F)/\tau. \qquad (2)$$

Comparison of k_r and k_{nr} reveals that substitution with the arylethynyl groups accelerates radiation process, while radiationless process from excited state is suppressed in this order, resulting in higher quantum yields.[7] With these results in hand, emission spectra of some relevant tetrakis(arylethynyl)silanes were recorded in order to confirm the generality of the high quantum yield. Figure 2 shows emission profiles of four



Scheme 1. Structures of **1**–**5**.

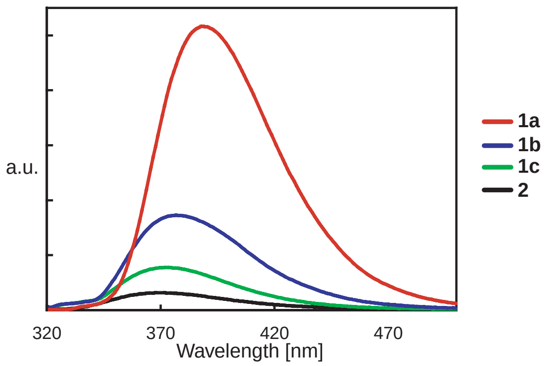


Figure 1. Emission of ethynylsilanes **1a**–**1c** and terminal acetylene **2** in CH_2Cl_2 (9.4×10^{-7} M).

Table 1. Photochemical data of **1a**–**1c** and **2**

	$\lambda_{max}{}^a$/nm	Δ^b/nm	$\Phi_F{}^c$	τ^d/ns	k_r/s^{-1}	k_{nr}/s^{-1}
1a	389	49	0.80	1.5	5.3×10^8	1.3×10^8
1b	377	44	0.68	1.4	4.9×10^8	2.3×10^8
1c	372	41	0.49	1.5	3.3×10^8	3.4×10^8
2	369	45	0.22	1.5	1.5×10^8	5.2×10^8

[a]Fluorescence in CH_2CH_2 (9.4×10^{-7} M). [b]Stokes shift. [c]Fluorescence quantum yields in CH_2Cl_2. Standard used was harmine ($\Phi_F = 0.45$ in 0.1 M H_2SO_4). [d]Fluorescence life time, solution degassed by freeze–pump–thraw cycles, 5.0×10^{-6} M in $CHCl_3$.

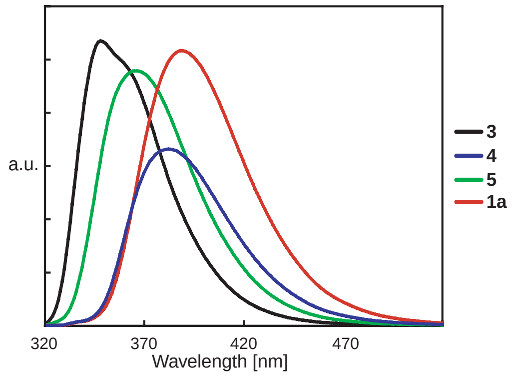


Figure 2. Emission of ethynylsilanes **3**–**5** and **1a** in CH_2Cl_2 (9.4×10^{-7} M).

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Table 2. Photochemical data of **3**, **4**, **5**, and **1a**

	λ_{max}[a]/nm	Δ[b]/nm	Φ_F[c]
3	350	24	0.83
4	383	44	0.90
5	368	39	0.98
1a	389	49	0.80

[a]Fluorescence in CH_2CH_2 (9.4×10^{-7} M). [b]Stokes shift. [c]Fluorescence quantum yields in CH_2Cl_2. Standard used was harmine ($\Phi_F = 0.45$ in 0.1 M H_2SO_4).

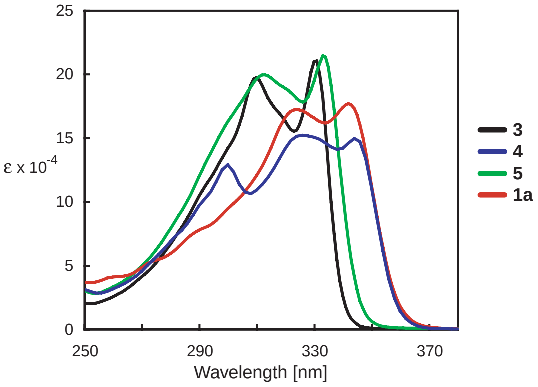

Figure 3. UV–vis spectra of ethynylsilanes **3**–**5** and **1a** in CH_2Cl_2 (3.5×10^{-5} M). Highest λ_{max}: 331 nm for **3**, 326 nm for **4**, 333 nm for **5**, and 325 nm for **1a**.

tetraethynylsilanes **3**, **4**, **5**, and **1a**, and the results are summarized in Table 2. All derivatives exhibited high quantum yields as expected. Unsubstituted **3** gave rise to an emission maximum at 350 nm with ambiguous vibronic structure at 360 nm. The methoxy group at the terminal phenyl ring induced a bathochromic shift of emission from that of **3**: *o*- **4** and *p*-derivatives **1a** underwent shifting by 33 and 39 nm, respectively, while *m*-derivative **5** did by 18 nm. In UV–vis spectra, similar bathochromic shift was observed, and *o*- **4** and *p*-derivatives **1a** exhibited larger shifts of highest λ_{max} than *m*-derivative **5** (Figure 3). The difference can be explained in terms of efficient electronic effect of ortho and para methoxy groups on the benzene ring through resonance. The same effect was reflected on the Stokes shifts of emission spectra, and thus **4** and **1a** have larger Stokes shift such as 44 and 49 nm, respectively, compared to 24 nm for **3**.

In conclusion, the effect of structural features of tetrakis(arylethynyl)silanes has been disclosed to enhance emission in terms of quantum yields. The enhancement can be explained in terms of enlarged reaction rate for emission. High quantum yields were observed in various tetrakis(arylethynyl)silanes. The characteristic features of tetraethynylsilanes would be versatile for designing emission materials. Further study on applications to EL devices is now underway.

We are grateful to Prof. S. Yamaguchi (Nagoya University) for helpful discussions. This work has been supported financially by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Published on the web (Advance View) October 14, 2006; doi:10.1246/cl.2006.1284