Unique Effects of 2,3,5,6,7,8-Hexasilabicyclo[2.2.2]octan-1-yl Moiety on Photophysical Properties of π-Conjugated System

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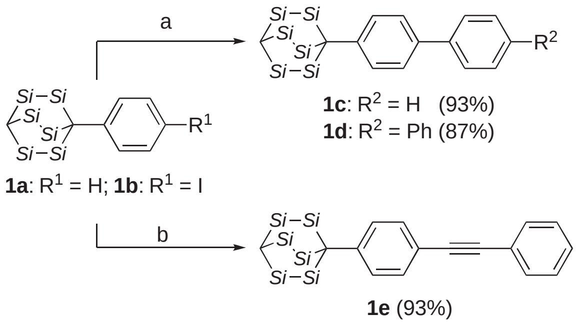
We prepared 2,3,5,6,7,8-hexasilabicyclo[2.2.2]octan-1-yl-substituted biphenyl, terphenyl, and tolan, and observed that introduction of the polysilacage group into arenes induced bathochromic shifts of absorption maxima and enhancement of molecular extinction coefficients, compared with the parent π-conjugated arenes, in addition to increase in fluorescence quantum yields.

Incorporation of a bicyclo[2.2.2]octane moiety into organic molecules induces molecular rigidity and enhances thermal stability. Therefore, such a bicyclic ring is often utilized as a core of liquid crystalline compounds[1] as well as a spacer between donor and acceptor moieties of molecular rods.[2] In these cases, functions of the cage framework are mainly based on the steric and insulating effect. On the other hand, UV spectra of 1-phenyl-2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane **1a** prepared by us suggested the possibility of σ–π electronic interaction between a hexasilabicyclo[2.2.2]octane moiety and a phenyl group at the bridgehead (Scheme 1).[3] Hence, the polysilacage group appears to act as a novel cage framework that induces not only steric but also electronic effects.[4] We report herein that synthesis, properties, and theoretical study of the polysilacage-substituted biphenyl **1c**, terphenyl **1d**, and tolan **1e**, focusing on unique electronic effects of the polysilacage group toward arenes.

A toluene solution of iodide **1b**[3b] with $C_6H_5B(OH)_2$ or 4-C_6H_5-$C_6H_4B(OH)_2$ in the presence of $Pd(PPh_3)_4$ (5 mol %) and NaOH aq was stirred at 80 °C for 12 h to give biphenyl **1c** or terphenyl **1d** in 93 or 87% yield, respectively.[5] Tolan **1e** was prepared from **1b** and phenylacetylene in the presence of $Pd(PPh_3)_2Cl_2$ (12 mol %) and CuI (21 mol %) in 93% yield. All products were colorless solids after purification by column chromatography on silica gel.



Scheme 1. Reagents and conditions (*Si* = $SiMe_2$): a) $C_6H_5B(OH)_2$ (1.2 equiv.) or 4-C_6H_5-$C_6H_4B(OH)_2$ (1.2 equiv.), $Pd(OAc)_2$ (6.5 mol %), PPh_3 (20 mol %), Na_2CO_3 aq, benzene, reflux. b) PhC≡CH (1.3 equiv.), $Pd(PPh_3)_2Cl_2$ (12 mol %), CuI (21 mol %), Et_2NH, rt.

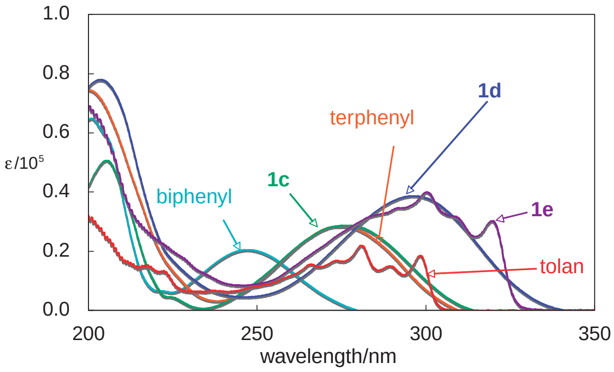


Figure 1. Absorption spectra of biphenyl, terphenyl, tolan, and **1c**–**1e** measured in cyclohexane (1.0×10^{-5} M).

Table 1. Photophysical parameters of biphenyl, terphenyl, tolan, **1a**, and **1c**–**1e**

Compound	λ_a/nm[a]	ε/$M^{-1}\,cm^{-1}$	λ_e/nm[b]	Φ_f
1a	241	17900	—[c]	—[c]
Biphenyl	247	20500	315	0.18
1c	274	28400	325	0.82
Terphenyl	276	28000	339	0.93
1d	298	38700	360	0.97
Tolan	298	18500	301	0.004
1e	320	30200	324	0.17

[a] λ_a: Absorption maximum of the longest wavelength. [b] Irradiation was effected with a UV light (λ = 265 nm), λ_e: emission maximum of the strongest fluorescence. [c] No emission was observed.

UV spectra of **1c**–**1e** measured in cyclohexane at room temperature are shown in Figure 1. Absorption maxima of **1c**–**1e** exhibited bathochromic shifts, compared with those of biphenyl, terphenyl, and tolan, respectively, as summarized in Table 1. Molecular extinction coefficients were enhanced by substitution of the cage group. Noteworthy is that absorption spectra of **1c** (green line) is almost identical to that of terphenyl (orange line), indicating that σ–π electronic interaction between a hexasilabicyclo[2.2.2]octane and a π-conjugated moiety is operative.[6]

Fluorescence spectra of **1c**–**1e** measured in cyclohexane are shown in Figure 2. Fluorescence quantum yields (Φ_f) of **1c**–**1e** were larger than those of the parent arenes, respectively (Table 1). Thus, the cage substitution was found to enhance Φ_f of arenes. Photophysical data for decay processes of **1c** and **1d** are summarized in Table 2. Incorporation of the cage moiety into biphenyl or terphenyl was found to shorten the decay time (τ). Thus, fluorescence radiative processes of the arenes were accelerated by the cage substitution.

Theoretical calculation of $HC(SiH_2SiH_2)_3C$-substituted biphenyl, terphenyl, and tolan (**1c′**–**1e′**) were carried out by

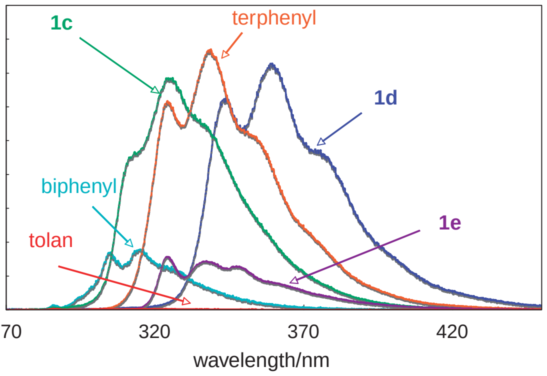


Figure 2. Fluorescence spectra of of biphenyl, terphenyl, tolan, and **1c**–**1e** measured in cyclohexane (1.0×10^{-5} M).

Table 2. Decay times (τ) and rate constants for fluorescence decay (k_f) and nonradiative decay (k_n) for biphenyl, terphenyl, **1c**, and **1d**

Compound	τ/ns	$k_f/10^7$ s^{-1}	$k_n/10^7$ s^{-1}
Biphenyl	16.0	1.1	5.1
1c	1.50	55	12
Terphenyl	0.95	83	23
1d	0.79	123	3.1

Table 3. HOMO and LUMO energies of biphenyl, terphenyl, tolan, **1c′**, **1d′**, and **1e′**

Compound	LUMO/eV	HOMO/eV	LUMO − HOMO /eV
Biphenyl	−0.68	−6.05	5.38
1c′	−0.92	−5.93	5.02
Terphenyl	−1.02	−5.78	4.75
1d′	−1.15	−5.73	4.58
Tolan	−1.25	−5.63	4.38
1e′	−1.37	−5.63	4.26

[a]Calculated at B3LYP/6-31G*//B3LYP/6-31G* level.

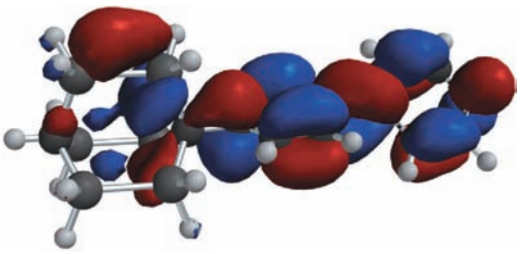


Figure 3. LUMO of **1c′**.

DFT method at B3LYP/6-31G*//B3LYP/6-31G* level (Table 3). Introduction of the cage moiety into the arenes lowered LUMO considerably and slightly raised HOMO, resulting in narrowing HOMO–LUMO gaps. The results are consistent with bathochromic shifts of absorption maxima. As shown in Figure 3, such lowering of LUMOs is presumably attributed to σ^*–π^* conjugation between π^* orbital of biphenyl and σ^* orbital of the Si–C$_{\text{bridgehead}}$ bond that aligned perpendicular to the phenyl ring.

In summary, we have demonstrated that 2,3,5,6,7,8-hexasilabicyclo[2.2.2]octan-1-yl group can be conjugated with π-conjugated system and alter their electronic structures. Further studies on preparation and properties of polysilacage compounds are in progress in our laboratory.

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5 **1c**: Mp 292 °C; R_f 0.24 (hexane); ^{1}H NMR (200 MHz): $\delta - 0.02$ (s, 1H), 0.27 (s, 18H), 0.29 (s, 18H), 7.2–7.7 (m, 9H); ^{13}C NMR (67.9 MHz): δ 0.6, 2.5, 3.6, 6.6, 126.1, 126.5, 126.6, 128.6, 130.8, 131.1, 140.6, 142.1; ^{29}Si NMR (53.6 MHz): $\delta - 21.2$, −20.4; IR (KBr): 3030, 2984, 2943, 2893, 2852, 1603, 1485, 1253, 1157, 1072, 968, 881, 856, 812, 735, 714, 692, 679 cm^{-1}; MS (FAB) *m/z* 526 (M$^+$), 527 (M$^+$ + 1); HRMS (FAB) Calcd for $C_{26}H_{46}Si_6$: 526.2215; Found 526.2213. **1d**: Mp 299 °C; R_f 0.12 (hexane); ^{1}H NMR (200 MHz): $\delta - 0.02$ (s, 1H), 0.27 (s, 18H), 0.30 (s, 18H), 7.3–7.8 (m, 13H); ^{13}C NMR (67.9 MHz): δ 1.1, 2.5, 3.6, 6.6, 126.0, 126.8, 126.9, 127.3, 128.7, 130.8, 131.1, 134.9, 139.3, 139.5, 140.6, 142.3; ^{29}Si NMR (53.6 MHz): $\delta - 21.1$, −20.3; IR (KBr): 3030, 2982, 2945, 2895, 2851, 1599, 1483, 1440, 1255, 1157, 1065, 968, 881, 814, 764, 746, 725, 712, 696, 679 cm^{-1}; MS (FAB) *m/z* 602 (M$^+$), 603 (M$^+$ + 1); HRMS (FAB) Calcd for $C_{32}H_{50}Si_6$: 602.2528; Found 602.2509. **1e**: Mp 296.5–297.0 °C; R_f 0.30 (hexane); ^{1}H NMR (500 MHz): $\delta - 0.024$ (s, 1H), 0.261 (s, 18H), 0.266 (s, 18H), 7.26–7.36 (m, 5H), 7.38–7.42 (m, 2H), 7.50–7.53 (m, 2H): ^{13}C NMR (67.9 MHz): δ 2.3, 3.0, 3.4, 22.2, 89.1, 89.6, 117.8, 123.7, 127.9, 128.3, 130.5, 131.0, 131.5, 144.1; ^{29}Si NMR (99 MHz): $\delta - 20.5$, −19.8; IR (KBr) 2941, 2895, 1595, 1506, 1256, 1161, 1136, 964, 858, 814, 752, 712, 679 cm^{-1}; MS (FAB) *m/z* 551 (M$^+$ + 1), 550 (M$^+$); HRMS (FAB) Calcd for $C_{28}H_{46}Si_6$: 550.2215; Found 550.2219.

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