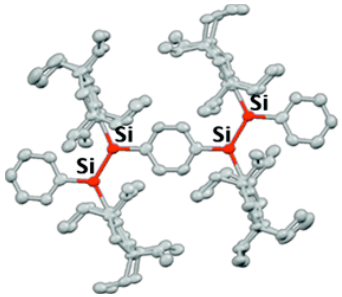
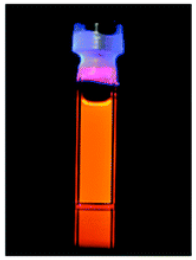
最先端有機元素化学②：最新論文からのトピックス

Coplanar Oligo(p-phenylenedisilenylene)s Based on the Octaethyl-Substituted s-Hydrindacenyl Groups
Fukazawa, A.; Li, Y.; Yamaguchi, S.; Tsuji, H.; Tamao, K.
J. Am. Chem. Soc. **2007,** *129*, 14164.





The silicon analogues of the oligo(p-phenylenevinylene)s (Si-OPVs) with highly planar structures have been synthesized using a newly developed ligand, the 1,1,3,3,5,5,7,7-octaethyl-s-hydrindacen-4-yl (Eind) group. Their X-ray crystal structures and spectroscopic data demonstrate that the π-conjugation effectively extends over the Si-OPV framework. Notably, tetrasiladistyrylbenzene exhibits an orange fluorescence even at room temperature both in solution and in the solid state, which is attributable to the effective extension of conjugation. To the best of our knowledge, the tetrasiladistyrylbenzene is the first emissive Si=Si derivative even at room temperature.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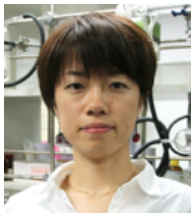
辻勇人
東京大学准教授


深澤愛子
名古屋大学助教

タイトルとTOCグラフィックから読み取れること

- OPV[oligo-(p-phenylenevinylene)]のケイ素誘導体の話
  Si=Si二重結合がベンゼンを挟んでいる
- Eind基という配位子が新しく合成された
- この化合物は溶液状態・固体状態でオレンジの蛍光を発する

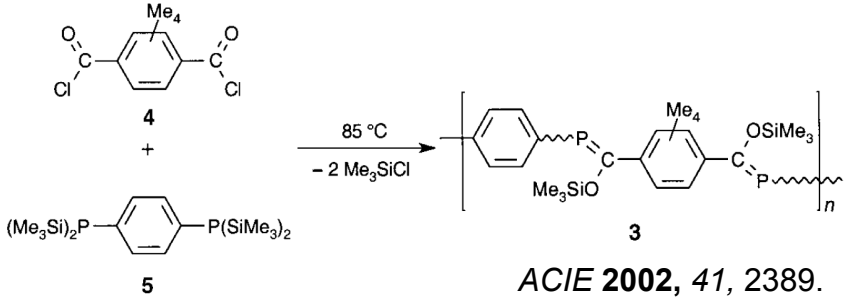
Introductionから読み取れること

- Si=C,P=P,Si=Siなどの重い二重結合はかさ高い置換基により安定化されてきた
- P=C, P=P, Si=Si, Ge=C, Ge=Geのオリゴマーやポリマーが合成されたが
  かさ高い置換基でπ共役系はねじれてしまっていた

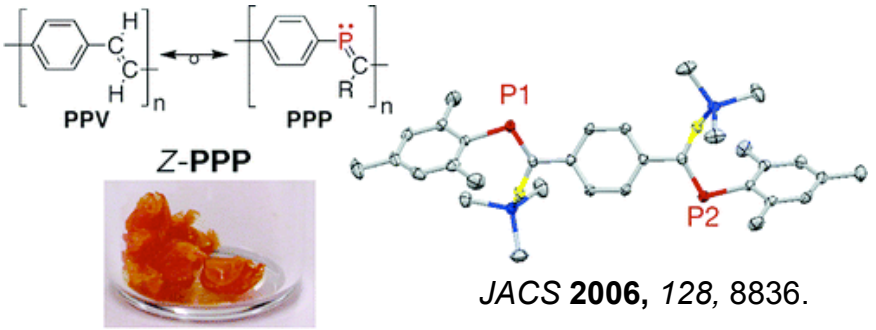
有機元素化学特論
第13回　2012.7.12

Oligomer and Polymer of Heavy Double Bond

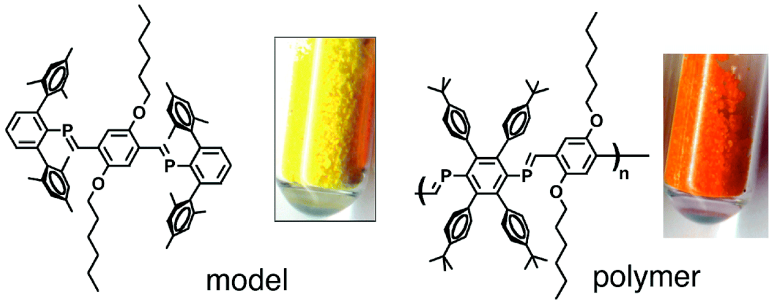
P=C polymer



ACIE **2002,** *41,* 2389.

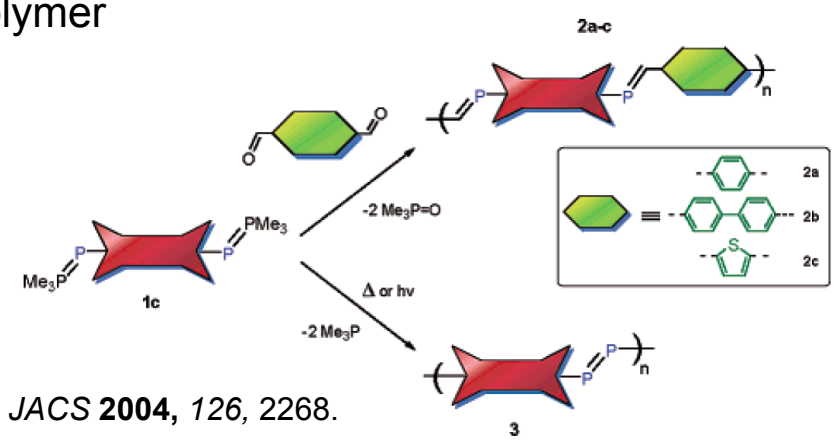


JACS **2006,** *128,* 8836.



Inorg. Chem. **2003,** *42,* 5468.

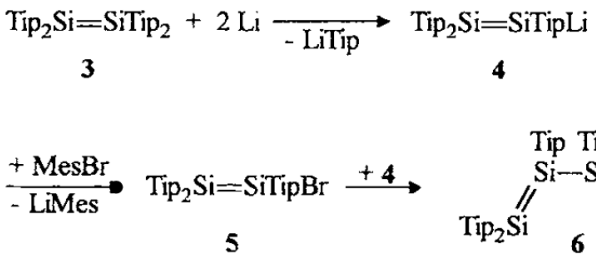
P=P polymer



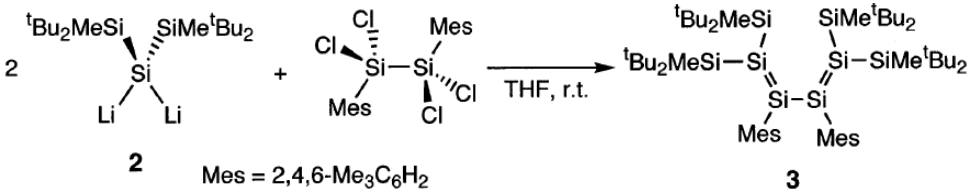
JACS **2004,** *126,* 2268.

Oligomers of Group 14 Double Bonds

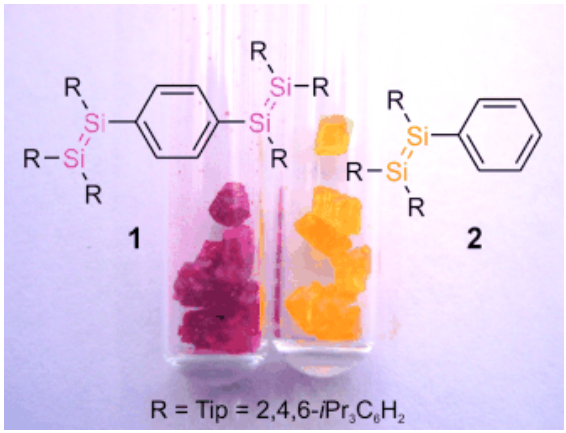
Conjugated Si=Si bonds



Tip = 2,4,6-*i*Pr$_3$C$_6$H$_2$; Mes = 2,4,6-Me$_3$C$_6$H$_2$ *ACIE* **1997,** *36,* 2503.

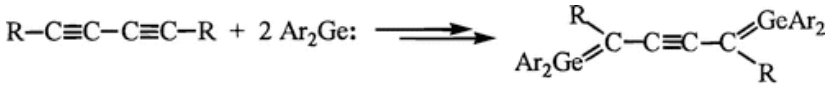


Organometallics **2004,** *23,* 3088.



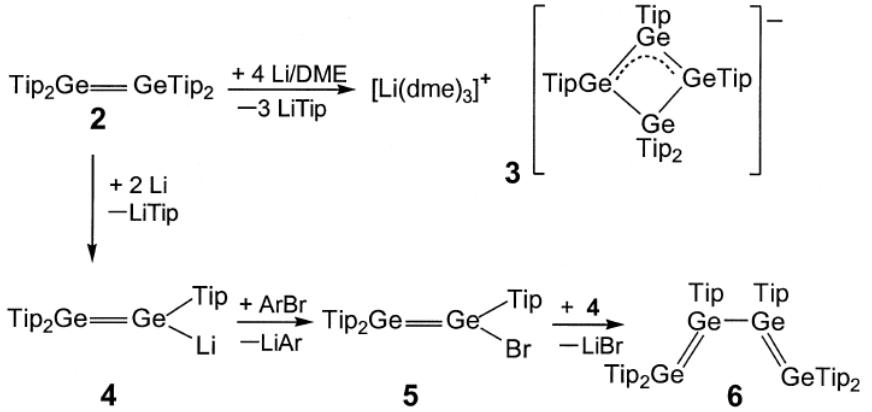
ACIE **2007,** *46,* 5783.

Conjugated Ge=C, Ge-Ge bond



Organometallics **2000,** *19,* 2835.

6a R = *n*C$_4$H$_9$
6b R = C$_6$H$_5$

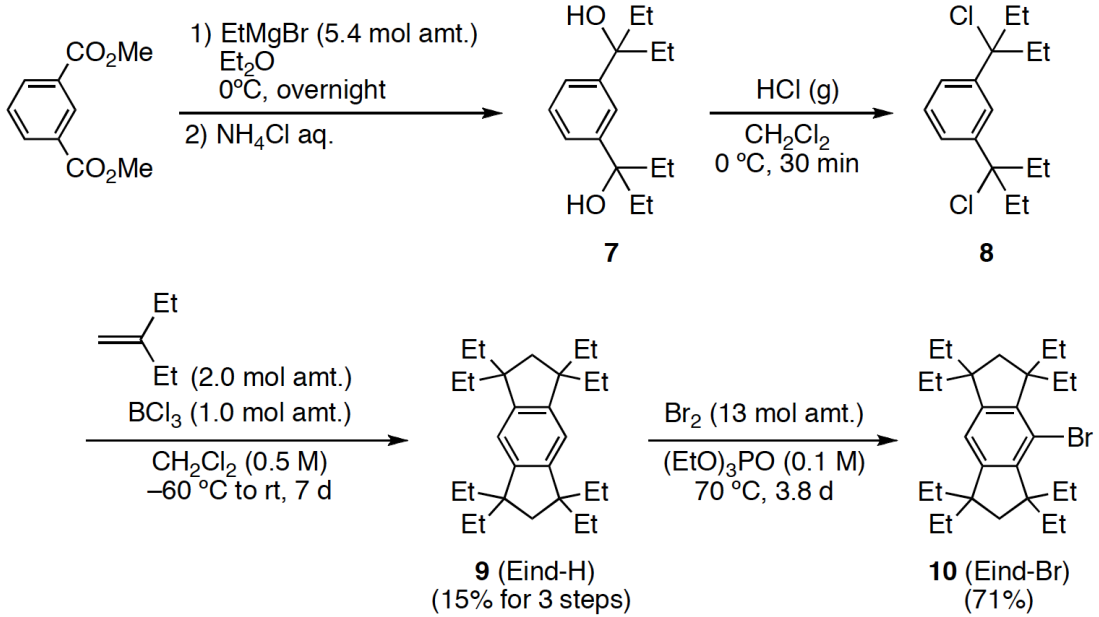


Scheme 1. Ar = 2,4,6-Me$_3$C$_6$H$_2$ (Mes), 2,4,6-*i*Pr$_3$C$_6$H$_2$ (Tip).

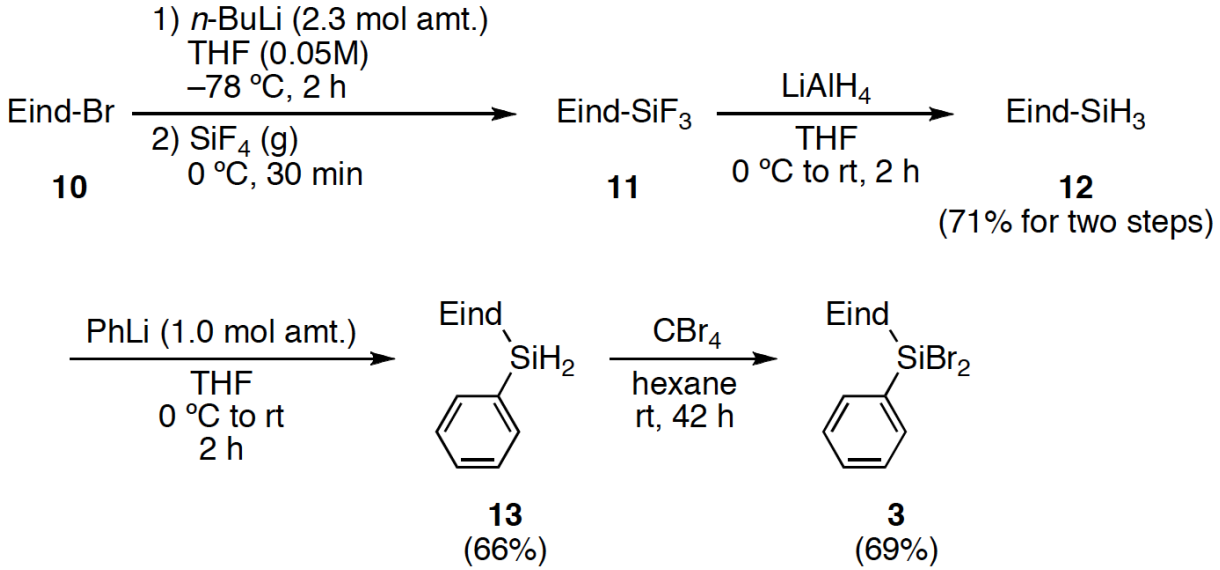
ACIE **2000,** *39,* 3703.

This Work 1: Synthesis of Dibromosilane 3

Synthesis of Eind-Br

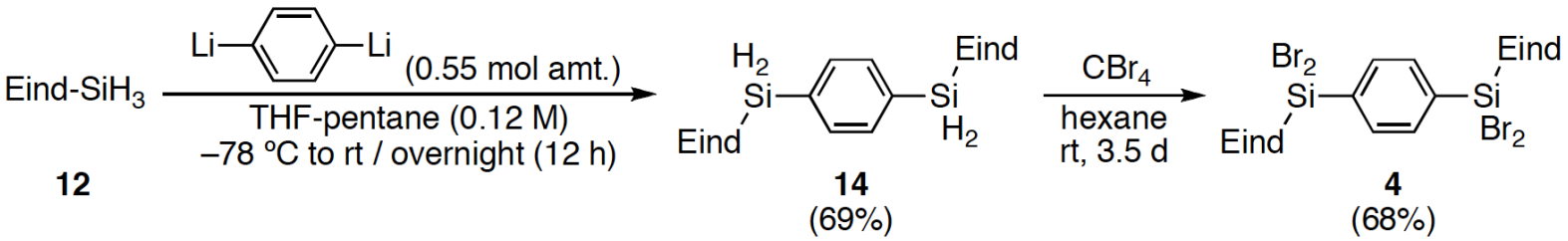


Synthesis of **3**

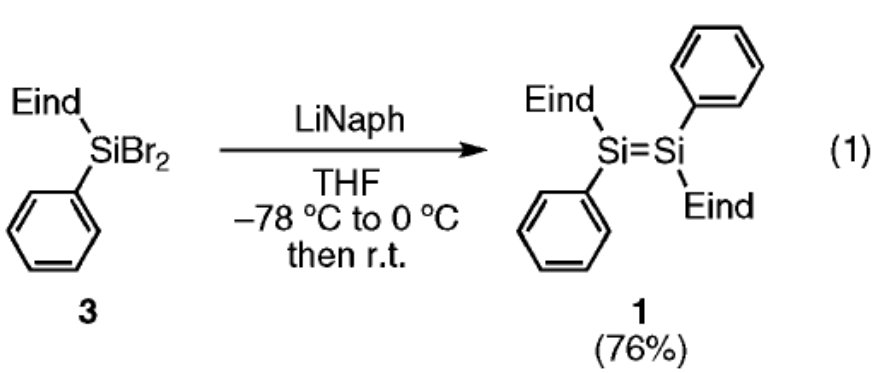


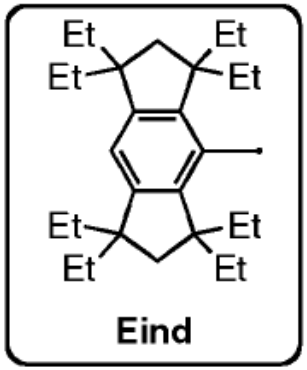
This Work 2: Synthesis of Disilene and Bis(disilene)

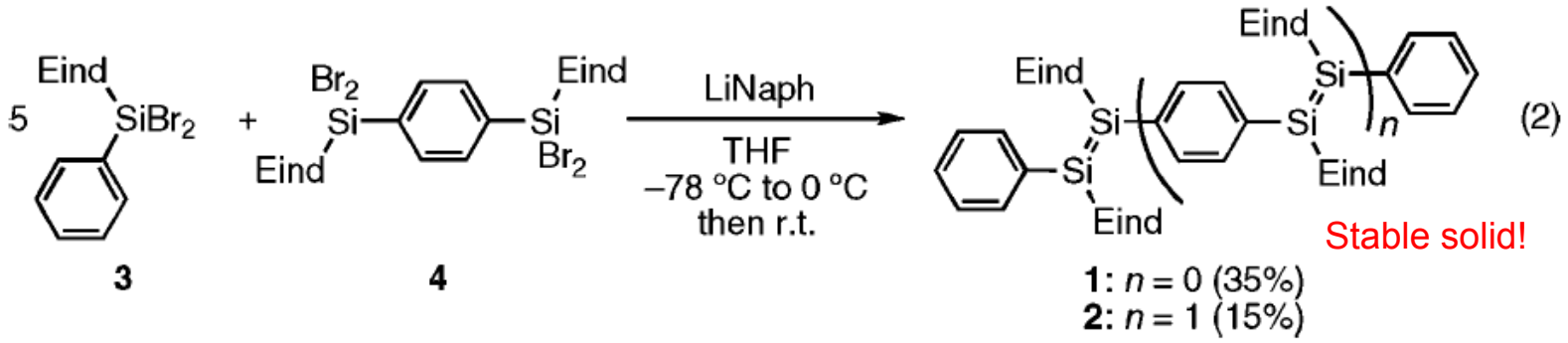
Synthesis of bis(dibromosilane) **4**



Synthesis of disilene **1** and bis(disilene) **2**

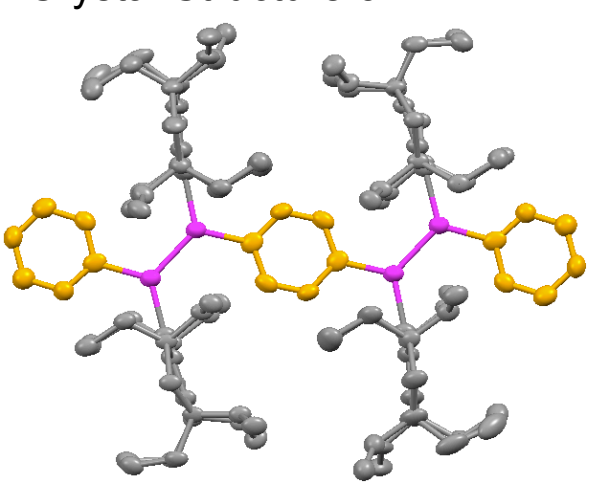


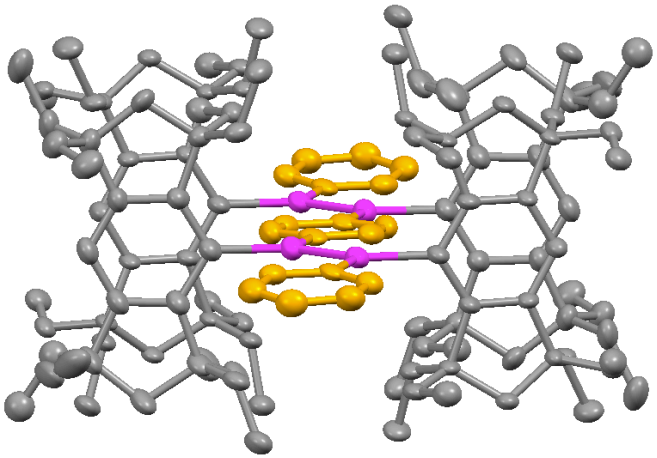


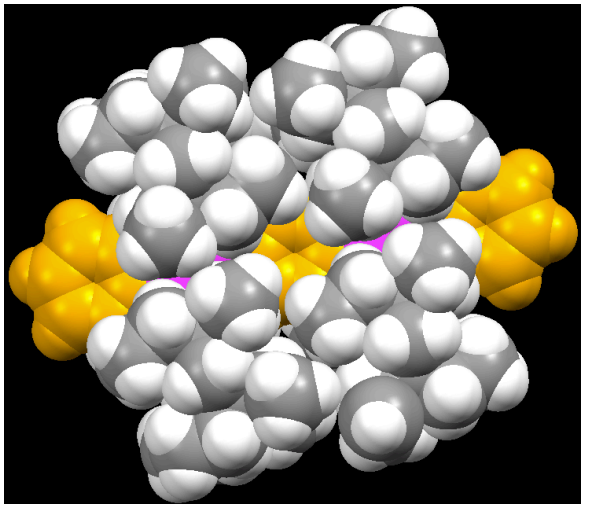


This Work 3: Crystal Structure of 2

Crystal Structure of **2**







真ん中のベンゼン環の中心にC_2対称軸が存在
=

Si−Si 2.156(2) Å
Si−C 1.860(6); 1.876(6); 1.911(5); 1.902(5) Å
Si周りの結合角の和=両方360°

This Work 4: Photophysical Properties of 2

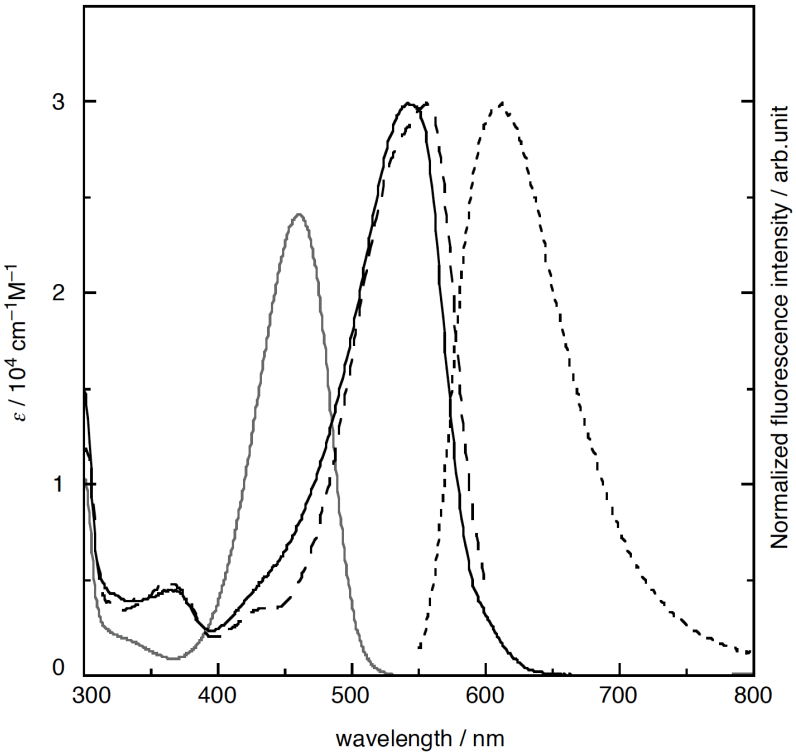


Figure S4. Electronic spectra of Si-OPVs **1** and **2** in *n*-hexane at ambient temperature.
UV-vis absorption of **1** (gray) and **2** (black solid line)
luminescence spectrum of **2** (black dotted line, excited at 460 nm)
excitation spectrum of **2** (black broken line, observed at 620 nm)

luminescence spectrum:

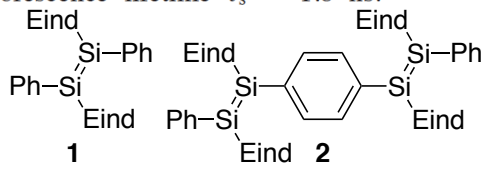
excitation spectrum:

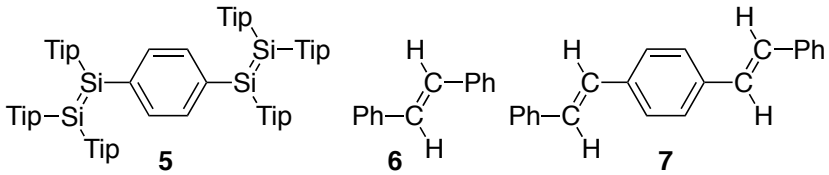
Table 1. Photophysical Data of Disilenes **1** and **2** and Related Compounds[a]

cmpd	UV–vis absorption λ_{max}/nm (ν_{max}/cm^{-1})	UV–vis absorption ϵ/cm^{-1} M^{-1}	fluorescence λ_{max}/nm (ν_{max}/cm^{-1})
1	461 (21700)	2.4×10^4	n.d.[b]
2	543 (18400)	3.0×10^4	612[c] (16300)
5[d]	508 (19700)	2.7×10^4	–
6[e]	295 (33900)	–	335 (29900)
7[f]	350 (28600)	–	385[g] (26000)

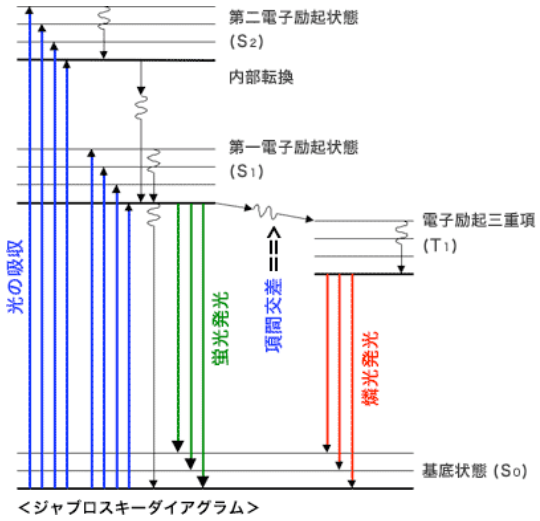
[a] Measured in *n*-hexane at room temperature. [b] Not detected. [c] Fluorescence quantum yield $\Phi_F = 0.10$, fluorescence lifetime $\tau_s = 1.8$ ns.

1 vs **2**:
5 vs **2**:
7 vs **2**, **6** vs **1**:





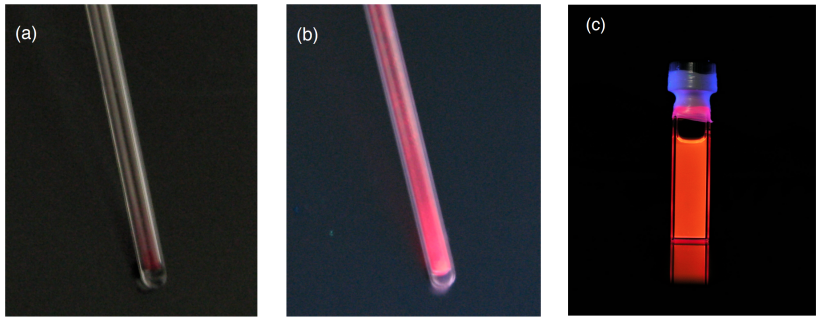
参考：蛍光発光のメカニズム
(Jablonski図)



<ジャブロスキーダイアグラム>

This Work 5: Luminescence and MOs

Figure S5. Photographs of compound **2**.
(a) solid in sealed tube in the dark
(b) solid under irradiation at 254 nm
(c) solution in hexane under irradiation at 254 nm



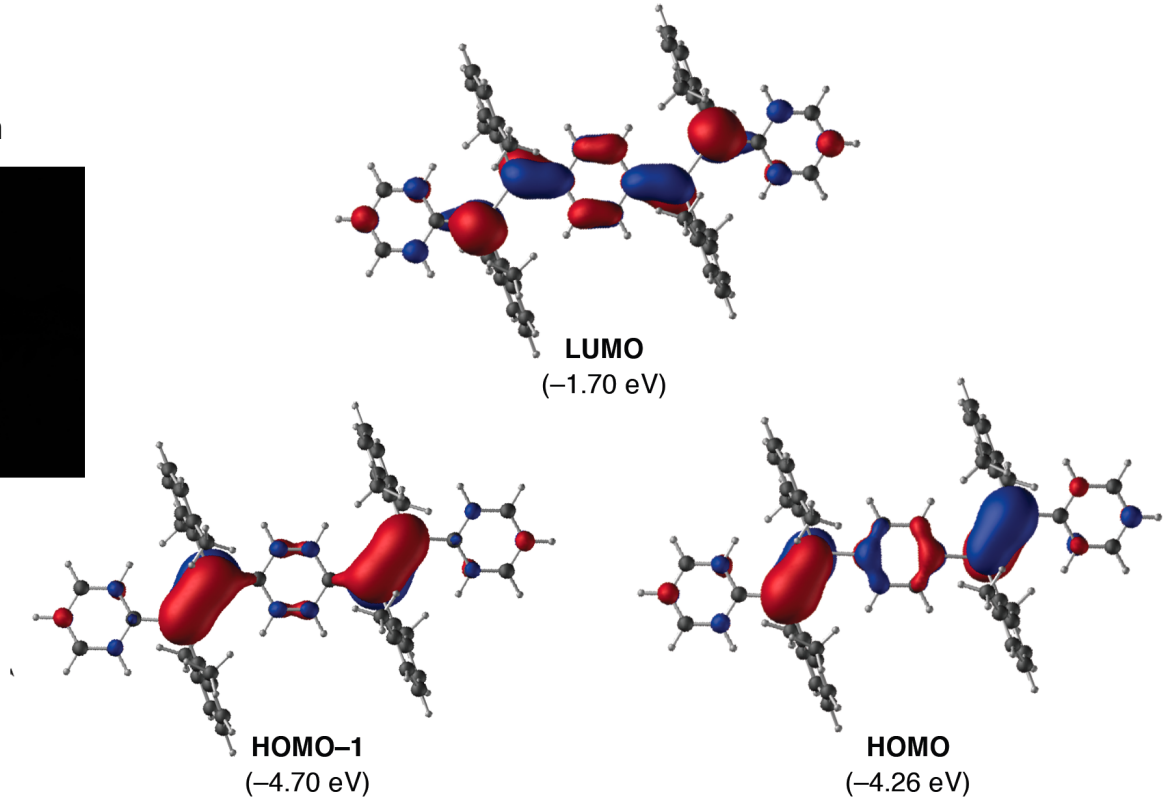


Figure S7. Plots of selected MOs of **2'** (isosurface at ± 0.03 a.u.).
計算レベルはB3LYP/6-31G(d)

次週の宿題 (古くて見られない参考文献は山下研webに置いてます)

Miyamoto, K.; Sei, Y.; Yamaguchi, K.; Ochiai, M.
"Iodomesitylene-Catalyzed Oxidative Cleavage of Carbon−Carbon Double and Triple Bonds Using m-Chloroperbenzoic Acid as a Terminal Oxidant"
J. Am. Chem. Soc. **2009,** *131*, 1382-1383.