J|A|C|S
COMMUNICATIONS

Synthesis and Reversible Control of the Fluorescent Properties of a Divalent Tin Dipyrromethene

Junji Kobayashi,* Tomokatsu Kushida, and Takayuki Kawashima*

*Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo,
Bunkyo-ku, Tokyo 113-0033, Japan*

Received June 2, 2009; E-mail: jkoba@chem.s.u-tokyo.ac.jp; takayuki@chem.s.u-tokyo.ac.jp

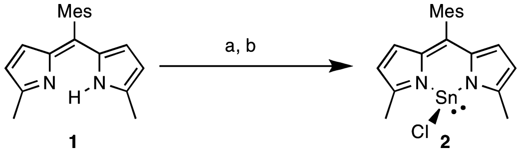
Stannylenes are heavy congeners of carbenes and have been widely investigated.[1] They easily dimerize without steric protection, and bulky substituents are necessary to stabilize these species. An alternative strategy for stabilization is the utilization of intramolecular coordination by the introduction of anionic chelating ligands such as β-diketiminate, aminotroponiminate, or amidinate. By the introduction of these ligands, LSnCl-type compounds have been isolated.[2] Chloride is the reactive ligand and is easily replaced by other small, reactive ligands, such as alkoxide, amide, azide, triflate, and hydride.[3] The presence of these small, reactive ligands promotes valuable reactivities, such as the polymerization of lactide, the cyclization of isocyanate, and the hydrostannylation of carbon dioxide.[4] These are interesting and important examples of applications of divalent tin compounds. However, they are limited to transformations on the tin atom, and the ligand functions only as a stabilizing group. On the other hand, Driess and co-workers[5] developed the ambivalent reactivity of silylene and germylene by using hydrohalogenated β-diketiminate ligand. These examples are very striking because they indicate that modification of the ligand could attach new functionality to the divalent group 14 species.

In this context, we focused our attention on dipyrromethenes as ligands of stannylenes. When these ligands are introduced to a boron atom or transition metals, they gain excellent optical properties.[6] We considered that the combination of the highly reactive stannylene with the fluorescent dipyrromethene ligand could produce a novel chromophore responsive to external stimuli. Here we report a novel stannylene bearing the dipyrromethene ligand and reversible control of its fluorescent properties by simple reactions on the tin atom.

A stannylene bearing a dipyrromethene ligand was readily synthesized by the reaction of an in situ-generated lithium dipyrrinato[7] with $SnCl_2$ (Scheme 1). SnClDIPY (**2**) was obtained as an orange solid in 74% yield. Compound **2** is relatively stable in air in the solid state, although it decomposed gradually in solution under the open atmosphere. The ^{119}Sn NMR spectrum of **2** showed a signal at −246.7 ppm corresponding to the divalent tin atom, which suffered from intramolecular coordination.[2]

The structure of **2** was determined by X-ray crystallographic analysis. The ORTEP drawing of **2** is shown in Figure 1a.[8] The tin center adopts a pyramidal structure, which is fairly common in Sn(II) chemistry.[2] The bond lengths and angles around the tin atom are listed in the Supporting Information and are not much different from those of similar Sn(II) compounds. There is an intermolecular interaction between the tin and chlorine atoms. Thus, the tin atom takes a pseudo-trigonal-bipyramidal structure, and **2** forms infinite columns along the *b* axis of the unit cell, as shown in Figure 1b.

Scheme 1. Synthesis of SnClDIPY (**2**)[a]



[a] (a) *n*-BuLi (1.0 equiv), −78 °C, THF; (b) $SnCl_2$ (1.0 equiv), r.t. (74% over two steps).

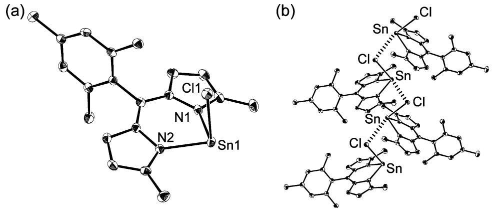


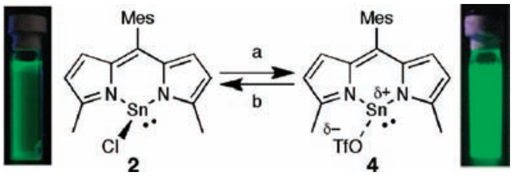
Figure 1. (a) ORTEP drawing of **2** (50% probability). (b) Packing structure of **2**. For selected distances and angles, see the Supporting Information.

The optical properties of **2** in benzene solution were investigated, and the data are summarized in Table 1. Compound **2** showed a strong absorption at 509 nm with vibrational structure, and BODIPY (**3**), bearing the same ligand, showed quite similar absorption properties ($\lambda_{max} = 514$ nm). On the other hand, a distinct difference in the fluorescence properties was revealed. Steady-state fluorescence emission of **2** was observed at 518 nm with a small Stokes shift. However, its quantum yield was 0.04, which is considerably smaller than that of **3** ($\Phi_f = 0.89$; $\lambda_f = 525$ nm).

To clarify the reason for the difference in the fluorescence properties of SnClDIPY and BODIPY, DFT calculations (B3LYP) were performed using model compounds[9] in which the mesityl group was replaced by a xylyl group and the methyl groups on the dipyrromethene were removed. The HOMOs and LUMOs of BODIPY and SnClDIPY consist of π and π^* orbitals, respectively, of the dipyrromethene framework, and their orbital shapes and energy levels are similar. The lowest-energy transitions of these species correspond to the HOMO−LUMO transitions. For SnClDIPY, however, the lone-pair (n) orbital of the divalent tin atom exists as the HOMO−1, and the energy difference between the HOMO and HOMO−1 is only 0.44 eV. Thus, the $n \rightarrow \pi^*$ transition should be located near the lowest-energy $\pi \rightarrow \pi^*$ transition and is considered to cause fluorescence quenching in SnClDIPY. If the energy level of the n orbital were to be decreased substantially, the resulting tin dipyrromethene compounds would be expected to gain good fluorescence properties. DFT calculations on the cationic species Sn^+DIPY predicted that the dipyrromethene π orbital still exists at a higher level (HOMO−2), whereas the n orbital lies at a much lower level (HOMO−6), so the energy difference between these two orbitals is increased to 2.02 eV. These predictions encouraged us to synthesize the cationic species in order to enhance the fluorescence emission.

10.1021/ja904470m CCC: $40.75

Scheme 2. Reaction of **2** with AgOTf[a]



[a] (a) AgOTf (1.0 equiv), r.t., toluene (89%); (b) Bu_4NCl (1.0 equiv), r.t., toluene (85% as estimated by ^1H NMR).

Chlorostannylenes have been reported to be easily converted to cationic tin species by silver salt metathesis.[3c] Indeed, the reaction of **2** with 1 equiv of AgOTf in toluene led to the quantitative formation of [SnDIPY][OTf] (**4**), which showed a bright-green fluorescence emission (Scheme 2). Compound **4** is an air- and moisture-sensitive orange solid. A signal for **4** was not observed in the ^{119}Sn NMR spectrum, but its structure was finally determined by X-ray crystallographic analysis. The ORTEP drawing of **4** is shown in Figure 2a.[10] In the crystalline state, the triflate ligand is attached to the tin atom as a bridging ligand, and **4** forms a polymeric chain (Figure 2b). The Sn−O distances varied from 2.420 to 2.534 Å, which are much longer than the sum of the covalent radii of Sn and O (2.14 Å), indicating that the Sn−O interactions are not strong.

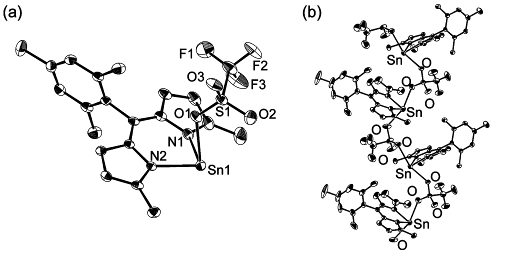


Figure 2. (a) ORTEP drawing of **4** (50% probability). (b) Packing structure of **4**. For selected distances and angles, see the Supporting Information.

UV−vis spectra of **4** showed a strong absorption maximum at 513 nm with a vibrational structure assignable to the $\pi \rightarrow \pi^*$ transition of the dipyrromethene framework. The absorption property of **4** was the same as that of **2**, indicating that the electronic structure of the dipyrromethene moiety of **4** was almost the same as that of **2**. However, **4** showed relatively strong fluorescence emission at 524 nm; its quantum yield was estimated as 0.42. Thus, the quantum yield of **4** was almost 10 times greater than that of **2**. As a preliminary examination, the reactions of **2** with other metal triflates [$Cu(OTf)_2$ and $Zn(OTf)_2$] were examined. However, no similar increases of fluorescence emission were observed. Moreover, **4** was easily transformed back to **2** in 85% yield (estimated by ^1H NMR) via treatment with Bu_4NCl, resulting in diminished fluorescence properties.

In summary, we have succeeded in synthesizing SnClDIPY (**2**) as a fluorescent stannylene. The fluorescence quantum yield of **2** was low compared with that of BODIPY. However, its fluorescence emission was reversibly controlled by the dechlorination and chlorination reactions. As a preliminary result, the increase of fluorescence emission was selective for AgOTf. Further investigation of applications of this molecular sensor is now under way.

Table 1. Optical Properties of Tin Dipyrromethenes **2** and **4** and BODIPY (**3**)[a]

	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_f (nm)	Φ_f [b]
2	509	8.54×10^4	518	0.04
3	514	9.71×10^4	525	0.89
4	513	6.46×10^4	524	0.42

[a] In benzene. [b] Absolute quantum yields.

Acknowledgment. This work was partially supported by the Global COE Program (Chemistry Innovation through Cooperation of Science and Engineering) and Scientific Research, MEXT, Japan. We thank Tosoh Finechem Corp. for the generous gifts of alkyllithiums.

Supporting Information Available: Experimental synthetic details and spectroscopic data for **2** and **4**, crystallographic data for **2** and **4** (CIF), computational details for the model compounds, and complete ref 9. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For reviews, see: (a) Takeda, N.; Tokitoh, N.; Okazaki, R. *Sci. Synth.* **2003**, *5*, 311. (b) Tokitoh, N.; Okazaki, R. *Coord. Chem. Rev.* **2000**, *210*, 251. (c) Driess, M.; Grützmacher, H. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 828. (d) Neumann, W. P. *Chem. Rev.* **1991**, *91*, 311.

(2) (a) Dias, H. V. R.; Jin, W. *J. Am. Chem. Soc.* **1996**, *118*, 9123. (b) Ding, Y.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Power, P. P. *Organometallics* **2001**, *20*, 1190. (c) Nimitsiriwat, N.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Dale, S. H.; Elsegood, M. R. J. *Dalton Trans.* **2007**, 4464.

(3) (a) Akkari, A.; Byrne, J. J.; Saur, I.; Rima, G.; Gornitzka, H.; Barrau, J. *J. Organomet. Chem.* **2001**, *622*, 190. (b) Ayers, A. E.; Klapötke, T. M.; Dias, H. V. R. *Inorg. Chem.* **2001**, *40*, 1000. (c) Ayers, A. E.; Dias, H. V. R. *Inorg. Chem.* **2002**, *41*, 3259. (d) Pineda, L. W.; Jancik, V.; Starke, K.; Oswald, R. B.; Roesky, H. W. *Angew. Chem., Int. Ed.* **2006**, *45*, 2602.

(4) (a) Dove, A. P.; Gibson, V. C.; Marshall, E. L.; Rzepa, H. S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2006**, *128*, 9834. (b) Dove, A. P.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 283. (c) Foley, S. R.; Zhou, Y.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2000**, *39*, 924. (d) Jana, A.; Roesky, H. W.; Schulzke, C.; Döring, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 1106.

(5) (a) Driess, M.; Yao, S.; Brym, M.; van Wüllen, C.; Lents, D. *J. Am. Chem. Soc.* **2006**, *128*, 9628. (b) Driess, M.; Yao, S.; Brym, M.; van Wüllen, C. *Angew. Chem., Int. Ed.* **2006**, *45*, 4349.

(6) For reviews, see: (a) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1184. (b) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891. (c) Wood, T. E.; Thompson, A. *Chem. Rev.* **2007**, *107*, 1831. (d) Arbeloa, F. L.; Bañuelos, J.; Martínez, V.; Arbeloa, T.; Arbeloa, I. L. *Int. Rev. Phys. Chem.* **2005**, *24*, 339.

(7) Cipot-Wechsler, J.; Al-Sehikh Ali, A.; Chapman, E. E.; Cameron, T. S.; Thompson, A. *Inorg. Chem.* **2007**, *46*, 10947.

(8) Sheldrick, G. M. *SHELXS-97: Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

(9) Frisch, M. J.; et al. *Gaussian03*, revision D.02; Gaussian, Inc.: Wallingford, CT, 2004.

(10) Two independent molecules are contained in the unit cell. Only one of the two molecules is shown, since they have almost identical structure.

JA904470M