Fluorescent Tin(IV) Complexes with Schiff Base Ligands

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Five novel fluorescent Schiff base tin(IV) complexes of the type [$SnCl_3$(L)] were synthesized and their properties were investigated: the emission wavelengths range from bluish green to orange (λ_{max}: 492–545 nm). DFT calculation shows that the order of the magnitudes of HOMO–LUMO gaps is consonant with that of the emission wavelengths (λ_{max}) of the complexes, and good correlation was observed between reduction potentials in DMSO and the energies of LUMO.

Fluorescent compounds have attracted much attention of researchers because of their intrinsic interests and applications such as organic electroluminescence.[1] One of Schiff bases, 2-hydroxy-1-naphthaldehydene-8-aminoquinoline (HL1) has been used for the fluorometric measurement of Be,[2a] Cr,[2b] Mo,[2c] Pb,[2d] and Hg.[2e] However, no X-ray structure of compound composed of any one of the above metal ions and HL1 ligand has been reported, while the X-ray structure of HL1 was reported recently.[3] Although X-ray structures of V^{V}[4a] and Tc^{V}[4b] complexes with the ligands were reported, no description of fluorescence was noted.

We report here synthesis and characterization of five novel fluorescent Schiff base tin(IV) complexes: [$SnCl_3$(L1)] (**1**), [$SnCl_3$(L2)] (**2**), [$SnCl_3$(L3)] (**3**), [$SnCl_3$(L4)] (**4**), and [$SnCl_3$(L5)] (**5**), where HL2, HL3, HL4, and HL5 also are Schiff bases analogous to HL1 (Chart 1). They (**1**–**5**) show a wide range of emission from bluish green to orange, and we should be able to tune fluorescent properties through the appropriate combination of Schiff bases and tin metal. The structures of **1**, **3**, **5**, and HL2 were determined by X-ray crystallography.

Many reports have appeared of fluorescence of tin,[5a,5b] all of them, however, discuss only the aspect of the quantitative analysis of tin in solution. Thermochromism of a Schiff base tin(IV) complex [$SnCl_3(L6)(H_2O)$] (HL6: salicylidene-8-aminoquinoline) was reported, but no fluorescence was described.[6] Reports about X-ray structures and their fluorescence of tin complexes are very rare; to our knowledge, X-ray structures of organo–tin complexes[7] with fluorenecarboxylic acid ligands and tin–iridium complex[8a,8b] are only examples so far reported. Also, there are X-ray structural reports on tin(IV) complexes with 8-aminoquinoline ligand, but nothing is described on fluorescence.[9a–9c] It should be noted that the diphenyltin bis(hydroxyquinolinato) complex shows electroluminescent properties.[10]

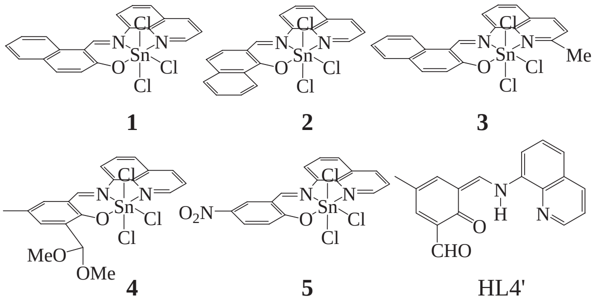

Chart 1.

HL1 was prepared according to the published procedures.[2c] Similar procedures were applied for the syntheses of other ligands, HL2, HL3, HL4′ (vide supra), and HL5. The novel tin complex **1** was synthesized by the following procedures: to a solution of HL1 (29.8 mg, 1.0×10^{-4} mol) in acetonitrile (20 mL) at 60 °C was added a solution of $SnCl_4 \cdot 5H_2O$ (36.0 mg, 1.0×10^{-4} mol) in acetonitrile (10 mL). Keeping the mixture at 60 °C overnight gave orange crystals of **1**: yield 20.9 mg (40%). Anal. Found (calcd for $C_{20}H_{13}Cl_3N_2OSn$): C, 46.26(45.98); H, 2.48(2.51); N, 5.50(5.36)%. Similar procedures to the synthesis of **1** were applied for the syntheses of other tin(IV) complexes, **2**–**5**.[11] Methanol was used for the synthesis of **2**, **4**, and **5**, and acetonitrile/methanol mixture was used for that of **3**. As for **4**, the aldehyde group of HL4′ changes to the acetal group on coordination to tin(IV).

X-ray structural analysis[12] of **1**, **3**, **5**, and HL2 revealed that the complexes adopt geometries close to octahedral ones: three chloride ions are coordinated meridionally. The structures of **2**, **4**, and HL4′ were determined by ^1H NMR spectroscopy (20 °C, 400 MHz, DMSO-d_6). Complexes **1** (yellowish green), **2** (orange), **3** (green), **4** (yellow), and **5** (bluish green) show fluorescence in DMSO (Figure 1), and the photophysical data are summarized in Table 1. Solid samples also show fluorescence at longer wavelengths. Data on solid states are also included in the table. The alteration of ligands led to fairly large emission wavelength shifts. This demonstrates that the emission wavelength of tin(IV) complexes is tunable by ligand modification.[1c,13] The emission wavelengths (λ_{max}) of the fluorenecarboxylato tin complexes are 355 and 390 nm,[7] and that of the tin–iridium complex is 645 nm,[8a,8b] and the emission wavelengths of the present Schiff base tin complexes are between those of the two types of complexes.

DFT calculation (B3LYP/Sn, LanL2DZ; others, 6-31G**) shows that the order of the magnitudes of HOMO–LUMO gaps (**5** (3.34 eV) > **3** (3.15) > **1** (3.04) > **4** (3.02) > **2** (2.80)) is consonant with that of the emission wavelengths (λ_{max}) of the complexes and that good correlation was observed between the energies of LUMO and reduction potentials in DMSO (Figure 2).[14]

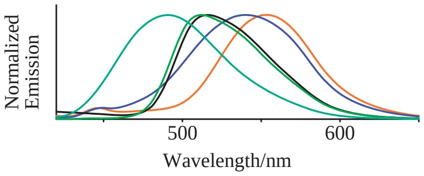

Figure 1. Emission spectra of **1** (—), **2** (—), **3** (—), **4** (—), and **5** (—) in DMSO at room temperature. ($\lambda_{ex} = 390$ nm).

Table 1. Photophysical data of **1**–**5** at room temperature

Compd	Absorbance $\lambda_{\mathrm{max,nm}}$ (ε/M^{-1} cm^{-1})	Emission	
		soln (QY)[a,b]	solid[c]
1	366 (9340), 453 (17700)	515 (0.30)	555
2	360 (16600), 470 (16200)	545 (0.015)	586
3	363 (9620), 450 (18000)	509 (0.18)	546
4	347 (15300), 435 (11700)	538 (0.030)	563
5	402 (14900)	492 (0.037)	523

[a] Emission $\lambda_{\mathrm{max,nm}}$ (quantum yield, QY) in a DMSO solution: 2.6×10^{-6} mol/L, $\lambda_{\mathrm{ex}} = 390$ nm. [b] Standard: a DMF solution of Alqn$_3$,[15] $\lambda_{\mathrm{ex}} = 390$ nm. [c] Emission $\lambda_{\mathrm{max,nm}}$.

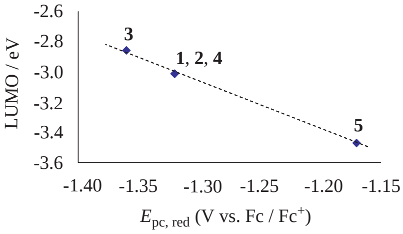

Figure 2. Plots of $E_{\mathrm{pc,red}}$ (V) vs. LUMO (eV) for **1**–**5**.

It should be noted that HL1, HL2, and HL3 are not fluorescent in DMSO, and formation of tin(IV) complexes leads to fluorescence,[16] though components of HOMO and LUMO and near those of the complexes **1**–**5** consist mainly of atomic orbitals of Schiff base ligands.[17]

It is very difficult to predict suitable combination of ligands and metals for the occurrence of fluorescence at present, and we expect to find the combinations experimentally. Further work on tin(IV) and other metal complexes with these and relevant ligands including 8-aminoquinoline is in progress to expand the emission wavelength span and to enhance the fluorescence quantum yields.[18,19]

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References and Notes

1 a) *Organic Electroluminescence*, ed. by Z. H. Kafafi, CRC Press, **2005**. b) C. H. Chen, J. Shi, *Coord. Chem. Rev.* **1998**, *171*, 161. c) S. Minakata, S. Moriwaki, H. Inada, M. Komatsu, H. Kajii, Y. Ohmori, M. Tsumura, K. Namura, *Chem. Lett.* **2007**, *36*, 1014. d) J. Yoshino, N. Kano, T. Kawashima, *Chem. Commun.* **2007**, 559.

2 a) C. Jiang, F. He, *Spectrochim. Acta, Part A* **2003**, *59*, 1321. b) C. Jiang, H. Wang, J. Wang, *Anal. Lett.* **2001**, *34*, 1341. c) C. Jiang, J. Wang, F. He, *Anal. Chim. Acta* **2001**, *439*, 307. d) H. Wang, F. He, C. Jiang, *Analyst* **2001**, *126*, 1164. e) J. Li, F. He, C. Jiang, *Anal. Sci.* **2006**, *22*, 607.

3 G. Sakane, H. Kawasaki, T. Shibahara, *Acta Crystallogr., Sect. E* **2006**, *62*, o2736.

4 a) G. Asgedom, A. Sreedhara, J. Kivikoski, E. Kolehmainen, C. P. Rao, *J. Chem. Soc., Dalton Trans.* **1996**, 93. b) F. Tisato, F. Refosco, A. Moresco, G. Bandoli, U. Mazzi, M. Nicolini, *J. Chem. Soc., Dalton Trans.* **1990**, 2225.

5 For example, a) Y. Yamamoto, Y. Dohdan, K. Morishige, Y. Nishikawa, *Nippon Kagaku Kaishi* **1990**, 25. b) S. Rubio, A. Gomez-Hens, M. Valcaecel, *Analyst* **1985**, *110*, 43.

6 A. M. Donia, H. El-Boraey, *Thermochim. Acta* **1994**, *237*, 195.

7 V. Chandrasekhar, P. Thilagar, A. Steiner, J. F. Bickley, *Chem.—Eur. J.* **2006**, *12*, 8847.

8 a) A. L. Balch, M. M. Olmstead, D. E. Oram, P. E. Reedy, Jr., S. H. Reimer, *J. Am. Chem. Soc.* **1989**, *111*, 4021. b) A. L. Balch, B. J. Davis, M. M. Olmstead, *Inorg. Chem.* **1990**, *29*, 3066.

9 a) T. Seifert, W. Storch, M. Vosteen, *Eur. J. Inorg. Chem.* **1998**, 1343. b) A. Hazell, K. F. Thong, J. Ouyang, L. E. Khoo, *Acta. Crystallogr., Sect. C: Cryst. Struct. Commun.* **1997**, *53*, 1226. c) A. Bengston, N. K. Goh, A. Hazell, L. E. Khoo, J. Ouyang, K. R. Pedersen, *Acta Chem. Scand.* **1996**, *50*, 1020.

10 X. T. Tao, M. Shimomura, H. Suzuki, S. Miyata, H. Sasabe, *Appl. Phys. Lett.* **2000**, *76*, 3522.

11 **2**: yield: 8.3 mg (56%). Anal. Found (calcd for $C_{20}H_{13}Cl_3N_2OSn$)%: C, 46.04(45.98); H, 2.67(2.51); N, 5.26(5.36). **3**: yield: 7.1 mg (46%). Anal. Found (calcd for $C_{20}H_{13}Cl_3N_2O_3Sn$)%: C, 47.03(47.02); H, 2.86(2.82); N, 5.21(5.22). **4**: yield: 8.3 mg (64%). Anal. Found (calcd for $C_{20}H_{19}Cl_3N_2OSn$)%: C, 42.32(42.86); H, 3.20(3.42); N, 5.08(5.00). **5**: yield: 54.8 mg (73%). Anal. Found (calcd for $C_{16}H_{10}Cl_3N_3O_3Sn$): C, 37.02(37.15); H, 1.78(1.95); N, 7.98(8.12)%.

12 Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary: No. 656122, **1**; 656123, **3**; 661505, **5**; 656124, HL2.

13 C. Pérez-Bolivar, V. A. Montes, P. Anzenbacher, Jr., *Inorg. Chem.* **2006**, *45*, 9610.

14 One electron reduction processes were observed in DMSO, and the reduction processes are irreversible. Oxidation of the complexes caused decomposition.

15 F. E. Lytle, D. R. Storey, M. E. Juricich, *Spectrochim. Acta, Part A* **1973**, *29*, 1357.

16 HL4′, which turns to L4 on coordination to tin(IV), is fluorescent. HL5 is unstable in DMSO.

17 The main components of HOMOs of **1**–**5** are the aldehyde moieties of the ligands and those of LUMOs are the quinoline moieties, therefore the electronic configuration of the emitting states can be assigned to charge transfer within the ligands.

18 Presented at the 57th Symp. on Coordination Chemistry of Japan, Nagoya, September 25–27, **2007**, Abstr., No. 1Fa-15.

19 Supporting Information is available electronically on the CSJ-Journal web site, http://www.csj.jp/journals/chem-lett/.

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