Novel Photochromic System Involving Organostannyl Compounds and 2-Aminomethylpyridine

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(Received November 18, 1997; CL-970876)

Photochromic behavior of organostannyl complexes was studied. The addition of 2-aminomethylpyridine to Sn(IV)R_nX_{4-n} (n=1~3) resulted in a reddish purple coloration and it showed the character of photochromism.

Organostannyl compounds have been used as the evasive material in paint and catalysts for plastic production.[1,2] In organic synthesis, the organostannyl group has been used as synthetic reagents as well as organosilyl groups.[3,4] Furthermore, the homoletic tin(II) compounds SnRx have two free P orbitals and one unpaired electron.[5] This organostannyl compounds act as both an electron donor and an electron acceptor because of their unique electron distribution. Leung and his co-workers reported the structure about novel donor-acceptor complex between two tin centers based on the single crystal X-ray analysis.[5]

Spiropyrane and fulgide are well known as compounds which show the photochromism.[6-10] These compounds have attracted considerable interests in the application for light-triggered molecular devices.[11] Many organic compounds have received attention due to their photochromic behavior in solution and solid state, in contrast, the photochromic compounds containing organometals have rarely been reported. In this communication, we present strong coloration and photochromic behavior by the organostannyl compounds Sn(IV)R_nX_{4-n} (R=alkyl, phenyl, X=F , Cl , Br , I , CH_3COO , n=1~3) and 2-aminomethylpyridine(2-AMPy). We found that the mixture of Sn(IV)R_nX_{4-n} and 2-AMPy result in a reddish purple coloration, while each are solved in almost solvents and their solution show no color. As an example, the visible spectra of dibutyltindiacetate(DBTDAc), 2-AMPy, and their mixture are shown in Figure 1. The mixture has two strong absorption maxima at 390nm (log ε =3.57) and 572nm(log ε =4.30).

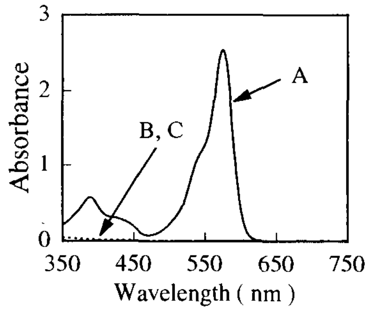

Figure 1. UV-Vis absorption spectra of the mixture between DBTDAc and 2-AMPy;
A: mixture, B: DBTDAc (1.25×10^{-4} $moll^{-1}$),
C: 2-AMPy (5.0×10^{-4} $moll^{-1}$).

Table 1. Molar extinction coefficient ε at λ_{max} in acetonitrile

Run	Sn(IV)R_nX_{4-n}	Ligand	λ max	Log ε
1	Sn(n-Bu)$_2$(CH_3COO)$_2$	2-AMPy	572	4.330
2	Sn(n-Bu)Cl_3	”	600	4.362
3	Sn(n-Bu)$_2$$Cl_2$	”	572	4.301
4	Sn(n-Bu)$_3$Cl	”	572	4.000
5	Sn(n-Bu)$_4$	”	-	--
6	Sn(n-Bu)$_3$F	”	572	2.867
7	Sn(n-Bu)$_3$I	”	572	3.220
8	Sn(n-Bu)$_3$(CH_3COO)	”	572	3.091
9	Sn(Me)$_3$ Cl	”	572	3.820
10	Sn(Ph)$_3$Cl	”	572	4.445
11	Sn(Oct)$_3$Cl	”	572	4.506
12	$SnCl_2$	”	-	--
13	$SnCl_4$	”	-	--
14	Sn(n-Bu)$_2$$Cl_2$	en[a]	-	--
15	”	2-AMPi[b]	-	--
16	”	Pyridine	-	--
17	”	2,2'-Bipyridine	-	--
18	”	3-AMPy	-	--
19	”	4-AMPy	-	--

- No coloration, -- Calculation impossible
[a] Ethylenediamine, [b] 2-Aminomethylpiperidine.

Moreover, the mixture exhibits a strong fluorescence peak at 591nm by excitation at 397nm. However, other ligands such as ethylenediamine, 2,2'-bipyridine and 3- or 4-aminomethylpyridine(3-,or 4-AMPy) showed no coloration with Sn(IV)R_nX_{4-n}. It is well known that 2-AMPy is bidentate ligand and has a high chelate activity to transition metals.[12] The strong coloration will be brought about a formation of complex between Sn(IV)R_nX_{4-n} and 2-AMPy. Other organostannyl compounds were also examined and the tipical absorption peaks were summarized in Table. 1. The absorption maximum changed a little by the kinds of (R) and counter anions (X) in Sn(IV)R_nX_{4-n}. The length of alkyl groups affected molecular extinction coefficient(ε) and the absorption maximum. ε increased in proportion to the length of alkyl chains. Sn(n-Bu)$_1$(Cl)$_3$ and 2-AMPy exhibited a red shift of 28nm compared with the mixture of Sn(n-Bu)$_2$(Cl)$_2$ or Sn(n-Bu)$_3$(Cl) and 2-AMPy. It is noteworthy that the mixture of Sn(n-Bu)$_4$ and 2-AMPy exhibits no coloration. Furthermore, SnX_2 or SnX_4 out of organic group showed no coloration even if mixed 2-AMPy. These results show the structure of these complex were influenced by the presence of Sn-C bond and the length of alkyl chains. A colored solution is achromized by irradiation of visible light, and the initial color is recovered by thermal acceleration in the dark. Irradiation of visible light was carried out by the use of 300w tungsten lamp for 60 min at room temperature. Figure 2 shows the change of absorption spectra for the mixture of DBTDAc and 2-AMPy in 2-methoxyethanol. This leads to decrease of the electronic spectral absorption at 572nm. The absorbance change of the mixture was repeated 10 times by light-on and -off as also shown in Figure 2. This system shows the reversible

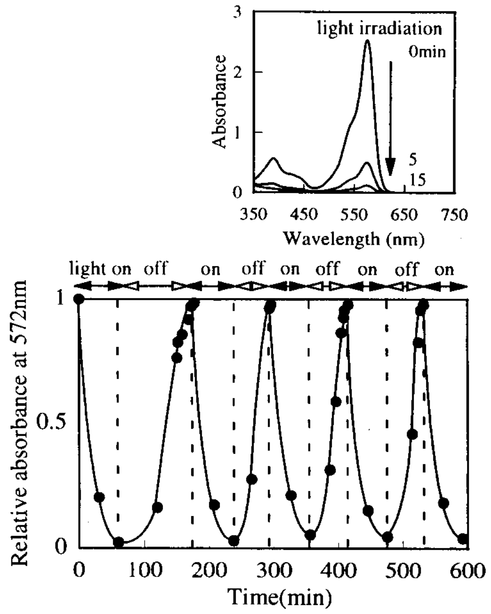

Figure 2. Repeated reversible property of the photochromic reaction for the mixture of DBTDAc and 2-AMPy in acetonitrile at 25 °C.

photochromic behavior.

In conclusion, the combination between SnR_nX_{4-n} and 2-AMPy shows the strong coloration with large ε and reversible photochromic behavior. The coloration suggests the formation of metal complex between SnR_nX_{4-n} and 2-AMPy. Further studies on the structure of complex are in progress.

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