Novel Fluorescent Aluminum Complexes Based on *N*-Hydroxy-3,6-diaryl-4-phenyl-2-pyridone Ligands

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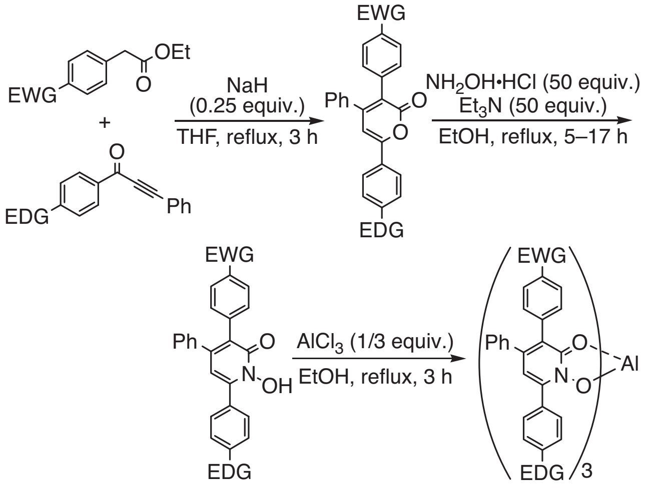
Novel fluorescent aluminium complexes of *N*-hydroxy-3,6-diaryl-4-phenyl-2-pyridone derivatives were synthesized and their fluorescent properties were investigated. The complexes having a trifluoromethyl group and a methoxy group at the para-position on the 3- and 6-phenyl groups exhibit purple fluorescence in the solid state.

Fluorescent organic compounds, especially organic electroluminescence (EL) devices, have attracted much interest because of applications such as large-area light-emitting displays that operate at low-drive voltage.[1] Thus, the development of new types of fluorophores; small organic molecures[2–4] as well as organic metal complexes,[5–11] has been actively pursued. For metal organic complexes, emission properties are readily controlled by a number of factors, including electronic properties of metal ions, ligands, and coordination length. One of the most representative emitting materials is Alq_3 [tris(8-hydroxyquinolinato)aluminum], which was originally reported by Tang's group in 1987.[5] This complex plays an important role as an electroluminophore and is the electron-transporting compound currently used in organic light-emitting diodes (OLEDs). In addition, metal–chelate materials having aromatic heterocycles and phenolic oxygen moieties have been reported. These compounds can be easily tuned by choosing a suitable ligand of the complexes.[7] Recently, elegant tuning of the emission of Alq_3 derivatives was achieved by the introduction of a variety of substituents at the 5-position of the ligand.[11]

On the other hand, the authors recently reported on a new series of fluorophores that consist of 6-membered heterocycles, pyrones[12–14] and pyridones[15] having triaryl subsituents at 3-, 4-, and 6-positions. These compounds exhibit intense fluorescence from blue to orange in the solid state, but this fluorescence is weak in solution. Because the nitrogen atom on the pyridones could have heteroatoms that would coordinate to metals, the authors hypothesized that the introduction of hydroxy groups to the nitrogen would newly form a metal-complex through a 5-membered chelating model including carbonyl oxygen.

This paper reports the formation of novel metal–chelate complexes (especially aluminum complexes), based on *N*-hydroxypyridone ligands, in which electron-withdrawing and donating groups were introduced at the para-position on 3- and 6-substituted phenyl rings. The photoluminescence properties of the complexes were studied, and blue and yellowish-green emitting materials were obtained.

The synthesis of aluminum complexes is shown in Scheme 1. 3,6-Diaryl-4-phenyl-α-pyrones, precursors of pyridones, were prepared from ethyl arylacetates and aroylphenylacetylenes in the presence of a catalytic amount of sodium hydride.[15,16] The pyridones were readily synthesized by the reaction of the pyrones with hydroxylamine hydrochloride in the presence of triethylamine.



Scheme 1. Synthesis of aluminum complexes.

These pyridones were converted to the corresponding aluminum complexes by reaction of ethanolic solutions of the *N*-hydroxypyridones with aluminum chloride, followed by crystallization from tetrahydrofuran and water. Table 1 listed the yields of the last step reaction and the spectroscopic properties in solution and in the solid state of the synthesized aluminum complexes.

The absorption spectra of the complexes were measured in dichloromethane (1.0×10^{-4} M). Although the absorption maxima of complex **2a**–**2c**, which had a methoxy group at the para-

Table 1. Yields and spectroscopic properties of Al complexes

Complex	EWG	EDG	Yield/%	λ_{abs}/nm[a]	In CH_2Cl_2 solution	In the solid state
					λ_{flu}/nm[a]	λ_{flu}/nm
1a	H	H	83	335	413	415
2a	H	OMe	60	339	413	417
2b	Br	OMe	80	334	417	421
2c	CF_3	OMe	72	333	414	416
3a	H	NMe_2	52	355	465	493
3b	Br	NMe_2	43	358	472	519
3c	CF_3	NMe_2	37	354	485	479
Alq_3	—	—	—	380	514	494

[a]In a solution of CH_2Cl_2 (1.0×10^{-4} M).

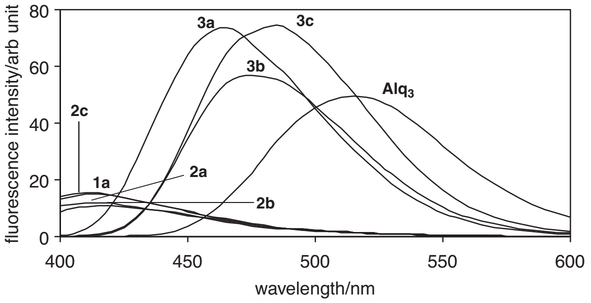


Figure 1. Fluorescence spectra of Al complexes in CH_2Cl_2 (1.0×10^{-4} M).

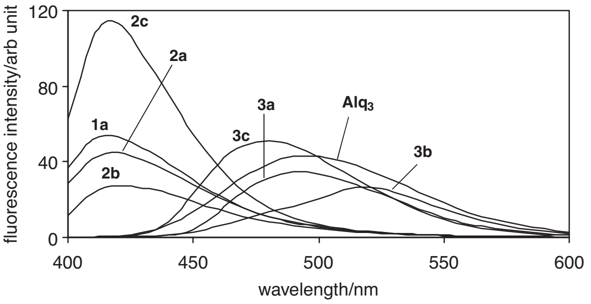


Figure 2. Fluorescence spectra of Al complexes in the solid state.

position on the 6-substituted phenyl ring as an electron-donating group, were almost the same as that of complex **1a**, the introduction of a dimethylamino group (**3a**–**3c**) induced a significant red-shift.

Complexes **1a** and **2a**–**2c** in dichloromethane solution had fluorescence maxima at approximately 415 nm and a weakly emitted blue fluorescence. However, complexes **3a**–**3c** had fluorescence maxima in the range of 465–485 nm and emitted green or yellowish-green fluorescence (Figure 1). The explanation for the red-shift might be that the strong electron-donating group decreased the torsion angle between the pyridone ring and the aryl groups at the 6-position of **3a**–**3c**.[13] The fluorescence quantum yields in solution of **3a**–**3c** were ca. 0.7, which is about three times higher than that of Alq_3 (Φ_f 0.2 in CH_2Cl_2 solution). In the solid state, complexes **1a** and **2a**–**2c** showed purple-blue fluorescence (Figure 2). The fluorescence quantum yield of complex **2c** (Φ_f 0.25) was rather low compared with that of Alq_3 (Φ_f 0.34 in the solid state).[17]

The emission spectrum of aluminum complex **1a** is shown in Figure 3. The EL device consists of an indium tin oxide (ITO) a transparent electrode, a 100-nm-thick layer of aluminum complex **1a**, and a 1-nm-thick CsF carrier injection layer, a Mg with silver electrode, and an Ag cap layer. The emission peaked at 450 nm, and the full width at half maximum (FWHM) of the emission peak was about 110 nm.[17]

In summary, novel fluorescent aluminum complexes of *N*-hydroxy-3,6-diaryl-4-phenyl-2-pyridones were synthesized and their spectroscopic properties were described. The complexes emit both in the solid state and in solution. The complex having a trifluoromethyl group and a methoxy group on the para-position at the 3- and 6-phenyl group exhibited purple fluorescence in the solid state, and the complex having a dimethylamino group on the para-position at the 6-phenyl group emitted yellowish-green fluorescence in a dichloromethane solution. Our group found a new type of metal complex fluorophore that emits blue fluorescence both in the solid state and in solution.

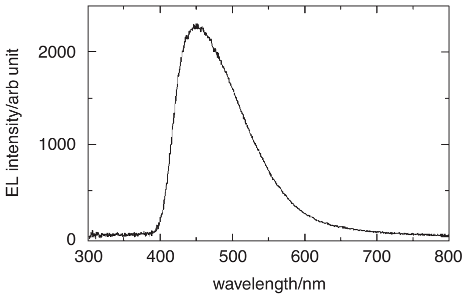


Figure 3. The emission spectrum of Al complex **1a**.

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

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