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Blue/green light-emitting diode based on diethyl[*N*-arylmethylenethiobenzahydrazonato]gallium complexes

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Three diethylgallium complexes of type Et_2GaL [L = *N*-(4-methoxy) benzylidenethiobenzahydrazonato (1), *N*-(4-*N*,*N*-dimethylamino)benzy lidenethiobenzahydrazonato (2) and *N*-(9-anthryl)methylenethio benzahydrazonato (3)] were synthesized by the reaction of triethylgallium with appropriate *N*-arylmethylenethiobenzahydrazones. The compounds obtained were characterized by elemental analysis, ^1H NMR, IR and mass spectroscopy, respectively. Monolayer light-emitting diodes based on the diethyl[*N*-arylmethylenethio benzahydrazonato]gallium doped poly(vinylcarbazole) were fabricated using a spin coating method. The photoluminescent and electroluminescent emission spectra of 1 and 3 were measured (429 and 479 nm for 1 and 3, respectively). The electroluminescent properties of 1 and 3 were also studied. The electroluminscence bands are located in the blue/green region (465 and 510 nm for complexes 1 and 3, respectively). Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: organogallium; *N*-arylmethylenethiobenzahydrazone; photoluminescence; electroluminescence

INTRODUCTION

Luminescent organic/organometallic compounds have attracted much attention recently due to their potential applications in electroluminescent displays (OLED).[1–14] Luminescent chelating complexes have been shown to be particularly useful in OLED because of their relatively high stability and volatility.[15] The best-known example of such chelating compounds is Alq_3 (q = deprotonated 8-hydroxyquinoline), a green emitter and an electron transporter in organic electroluminescence (EL) devices.[1–5,15] Blue luminescent compounds are among the most sought-after materials by scientists because they are one of the key color components required for full-color EL displays and are still rare. We reported recently some group 13 organometallic complexes produce a bright blue/green luminescence.[16–20] During our investigation of group 13 organometallic complexes, we discovered that some organogallium complexes have blue electroluminescent characteristics.[16] In order to study the influence of alkyl group bonded directly to metal on emitting wavelength, we chose triethylgallium reacting with *N*-arylmethylenethiobenzahydrazone, forming diethyl[*N*-arylmethyl enethiobenzahydrazonato]gallium complexes, thus providing us an opportunity to do a comparative study on the effect of substituent and electronic factors on luminescence of the complexes. Three novel diethylgallium complexes bearing *N*-arylmethylenethiobenzahydrazone have been synthesized and characterized. The details of syntheses, structures, photoluminescent and electroluminescent properties of these new complexes are reported herein.

EXPERIMENTAL

General procedure

All reactions were performed in a glove box under purified nitrogen. The solvents were refluxed with sodium benzophenone and distilled under nitrogen prior to use.

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The thiobenzhydrazones were prepared by condensation of thiobenzhydrazide with 4-methoxybenzaldehyde, 4-*N*,*N*-dimethylaminobenzaldehyde and 9-anthraldehyde, respectively. Triethylgallium was provided by the National 863 Program Advanced Material MO Precursors R&D Center of China. ^{1}H NMR spectra were recorded on a Bruker ARX-300 spectrometer with TMS as internal standard. Infrared spectra were collected on a Shimadzu IR 408 instrument in KBr pellets. Mass spectra were measured on a VG-ZAB-HS spectrometer (electron impact ionization). Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Luminescence spectra were measured on an AMINCO.BOWMAN luminance meter. Melting points were observed in sealed capillaries and were uncorrected.

Preparation of diethyl[*N*-(4-methoxy)benzylidenethiobenzahydrazo nato]gallium (1)

A solution of triethylgallium (0.32 g, 2 mmol) in 10 ml of cyclohexane was added dropwise over a period of 10 min with stirring to a solution of *N*-(4-methoxy)benzylidenethiobenzahydrazone (0.58 g, 2 mmol) in 10 ml cyclohexane and 2 ml of benzene mixture. After stirring the reaction mixture for an additional 30 min at room temperature, all volatiles were removed in an oil pump *in vacuo* and the yellow powder residue was recrystallized from a cyclohexane–benzene solution, giving **1** (0.685 g) in a yield of 86.3% based on TEGa.

Melting point: 48–50 °C. Anal. calcd for $C_{19}H_{23}N_2OSGa$ (397.18): C, 57.46; H, 5.84; N, 7.05. Found: C, 57.09; H, 5.85; N, 6.90. ^{1}H NMR data: 1.12 [t, 6 H, Ga(CH$_2$*CH$_3$*)$_2$], 0.61 [q, 4 H, Ga(*CH$_2$*CH$_3$)$_2$], 3.92 (s, 3 H, –*OCH$_3$*), 8.6 (s, 1 H, –*CH*=*N*), 6.9–8.2 (m, 9 H, *Ar-H*). IR data (cm^{-1}): 3046 (w), 2964 (w), 2933 (w), 2808 (W), 1603 (vs), 1513 (vs), 1461 (m), 1253 (vs), 1177 (vs), 1027 (m), 831 (m), 767 (m), 690 (s). MS data: 399 (8.2%), 397 (9.5%), 369 (2%), 367 (37%), 340 (1.4%), 338 (2.3%), 303 (14.5%), 301 (13.4%), 269 (11.4%), 237 (10.5%), 149 (99.2%), 135 (11.2%), 134 (100%), 133 (11.8%), 131 (19.9%), 129 (32.6%), 127 (47.9%), 121 (58.9%), 107 (13%), 104 (21%), 101 (7.9%), 99 (12%), 98 (11.7%), 91 (14.5%), 77 (17%), 71 (62.3%), 69 (97.7%).

Preparation of diethyl[*N*-(4-*N*,*N*-dimethylamino)benzylidenethio benzahydrazonato]-gallium (2)

Prepared as described for **1** from *N*-(4-*N*,*N*-dimethylamino) benzylidenethiobenzahydrazone (0.57 g, 2 mmol) and triethylgallium (0.32 g, 2 mmol). The compound was isolated as yellow crystal after recrystallization from benzene. Yield: 0.72 g (86.4% based on TEGa).

Melting point: 141–143 °C. Anal. calcd for $C_{20}H_{26}N_3SGa$ (410.23): C, 58.56; H, 6.39; N, 10.24. Found: C, 58.21; H, 6.14; N, 10.52. ^{1}H NMR: 0.6 [q, 4 H, Ga(*CH$_2$*CH$_3$)$_2$], 1.1 [t, 6 H, Ga(CH$_2$*CH$_3$*)$_2$], 3.1 [s, 6 H, –N(CH$_3$)$_2$], 8.8 (s, 1 H, –CH=N), 6.51–8.29 (m, 9 H, Ar-H). IR data (cm^{-1}): 3090 (w), 3049 (w), 2933 (m), 2895 (m), 2896 (m), 1614 (s), 1573 (vs), 1529 (vs), 1481 (s), 1439 (s), 1380 (s), 1248 (m), 1184 (s), 1182 (s), 930 (s), 812 (m), 684 (m). MS data: 410 (3%), 384 (3.9%), 383 (14.2%), 382 (70.3%), 381 (22.4%), 380 (97.2%), 190 (4.1%), 163 (6.1%), 162 (16.4%), 161 (39.2%), 160 (28.2%), 159 (8.2%), 148 (14.5%), 147 (100%), 146 (12.9%), 145 (20.5%), 134 (25.8%), 131 (14.4%), 130 (5.4%), 129 (42.7%), 128 (3.8%), 127 (66.9%), 121 (10.1%), 120 (14.7%), 119 (10.6%), 118 (9.7%), 105 (13.6%), 104 (16.7%), 103 (33.7%), 102 (5.3%), 101 (6.7%), 100 (5.2%), 99 (9.7%), 98 (6.9%), 77 (20.7%), 76 (13.8%), 71 (49.2%), 69 (78.9%).

Preparation of diethyl[*N*-(9-anthryl)methylenethiobenzahydra zonato]gallium (3)

Prepared as described for **1** from *N*-(9-anthryl)methylenethiobenzahy drazone (0.68 g, 2 mmol) and triethylgallium (0.32 g, 2 mmol). Compound **3** was isolated as yellow crystal after recrystallization from benzene. Yields: 0.80 g (85.6% based on TEGa).

Melting point: 167–169 °C. Anal. calcd for $C_{26}H_{25}N_2SGa$ (467.28): C, 66.83; H, 5.39; N, 5.99. Found: C, 66.23; H, 4.98; N, 5.46. ^{1}H NMR: 1.29 [t, 6 H, Ga(CH$_2$*CH$_3$*)$_2$], 0.81 [q, 4 H, Ga(*CH$_2$*CH$_3$)$_2$], 8.62 (s, 1 H, –CH=N), 7.43–8.32 (m, 12 H, Ar-H). IR data (cm^{-1}): 3055 (w), 3031(w), 1513 (m), 1588 (vs), 1477 (w), 1455 (m), 1415 (m), 1385 (m), 1358 (w), 1131 (m), 830 (s), 760 (s), 712 (s), 690 (m), 632 (m), 553 (s), 482 (s). MS data: 387 (0.35%), 308 (11.07%), 308 (47.38%), 307 (20.90%), 289 (2.1%), 288 (9.2%), 282 (12.2%), 281 (55.1%), 279 (11.9%), 252 (2.5%), 181 (45.6%), 155 (13.2%), 152 (35%), 153 (29.5%), 141 (5.8%), 135 (6.6%), 127 (100.0%), 103 (25.8%), 77.0 (25.9%), 71.0 (1.2%), 69 (4.3%).

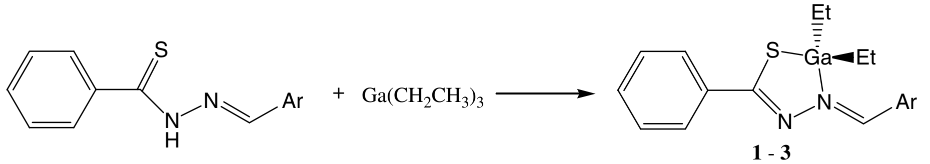
RESULTS AND DISCUSSION

Synthesis and characterization

Diethyl[*N*-arylmethylenethiobenzahydrazonato]gallium complexes (**1**, aryl = 4-methoxyphenyl; **2**, aryl = *p*-*N*,*N*′-dimethylaminophenyl; **3**, aryl = *N*-9-anthryl) were synthesized by the reaction of triethylgallium with *N*-arylmethylenethiobenzahydrazone, which could be obtained by the condensation of thiobenzahydrazine with aryldehyde in 1 : 1 molar ratio according to the general reaction (Scheme 1). The active hydrogen in *N*-arylethylenethiobenzahydrazone reacts rapidly at room temperature with triethylgallium in 1 : 1 stoichiometry, affording the corresponding diethyl[*N*-arylmethyl enethiobenzahydrazonato]gallium complexes in high yields.

Although triethylgallium is extremely moisture and oxygen sensitive, the complexes obtained are fairly stable on exposure to air. Compounds **1–3** could be left in ambient atmosphere for months without obvious decomposition. The complexes are nearly insoluble in cold saturated hydrocarbons such as pentane or petroleum and fairly soluble in benzene or toluene. All products obtained gave satisfactory elemental analysis results and have been characterized with ^{1}H NMR, IR and mass spectroscopy, respectively.

In the IR spectra of the complexes, the absence of N–H stretch vibration absorption verifies the reaction of the active hydrogen atom of the ligands with triethylgallium.



1 - 3

1: Ar = 4-methoxyphenyl
2: 4-*N*,*N*-dimethylaminophenyl
3: 9-*N*-anthryl

Scheme 1. Synthesis of complexes **1–3**.

It is also confirmed by absence of nitrogen-bonded proton signals in the ^1H NMR spectra of complexes. In IR spectra C–H stretch vibrations of the gallium-bonded ethyl groups are visible in the region of 2900–2950 cm^{-1}. In ^1H NMR spectra of the complexes, chemical shifts of the protons on metal-bonded carbon move downfield compared with triethylgallium, suggesting the electron-withdrawing nature of the thiobenzahydrazonyl group. Molecule ion peaks of the complexes **1–3** were all visible in their MS spectra. Relative intensity of the peaks of gallium-containing species agrees well with the isotopic distribution of the gallium atoms [^{69}Ga (ca. 60%); ^{71}Ga (ca 40%)].

Photoluminescence studies

Photoluminescence emission spectra of the complex **1** and **3** (solid state), for example, were measured as shown in Fig. 1. Complexes **1** and **3** produce a bright blue/green color in solution as well as in solid state upon irradiation by UV light. The emission maximum is at $\lambda = 429$ nm with an intensity of 43 a.u. for complex **1** and $\lambda = 479$ nm with an intensity of 132 a.u. The photoluminescence (PL) spectra powder samples of **1** as well as **3** match those films. The fact that compounds **1** and **3** have a similar emission band in solution, solid and films indicates that the luminescence observed in these complexes is a molecular property, attributed to the $\pi^* \rightarrow \pi$ transition of the *N*-arylmethylenethiobenzahydrazone ligands. The luminescence of complexes **1** and **3** is in sharp contrast to those of the free ligands which have a weak emission. The role of the central ion (Ga) in complexes is therefore simply to stabilize the negatively charged ligand via the formation of coordination bonds.[21,22] From Fig. 2, complex **1** exhibits relative weak photoluminescence intensity while complex **3** exhibits relatively stronger PL emission intensity. This may be attributed to the large delocalized conjugated anthryl ring. The relatively weak emission of complexes **1** may also be attributed to methoxy substituent on phenyl which may increases the thermal vibrations of the emitting, thus reducing the emission efficiency or the interference of π orbital on the delocalized conjugation system which could effectively quench the emission by intercepting the electrons returning from the excited state. It illustrates clearly that different substituents exerts different effects on photoluminescence characteristic.

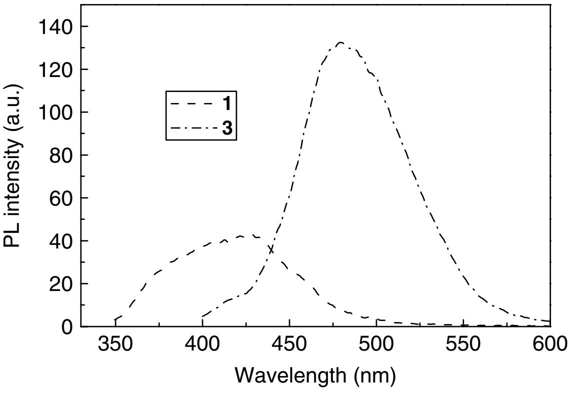


Figure 1. Photoluminescence spectra of **1** and **3** in solid state.

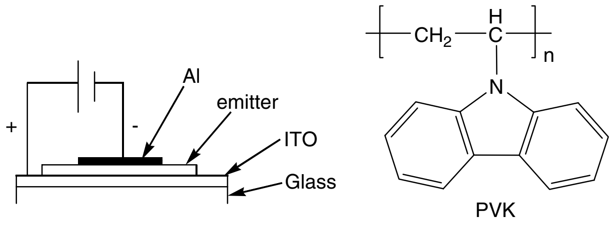


Figure 2. Configuration of devices and PVK structure.

Electroluminescence studies

The electroluminescence device structure is shown in Fig. 2. The gallium complexes were used as emitters. The complexes were dissolved in chloroform. The device was prepared on patterned indium–tin-oxide (ITO) coated on glass substrate, which was cleaned ultrasonically in a mixture of isopropyl alcohol and water (1 : 1) and degreased in toluene vapor, with a sheet resistance of near 80 $\Omega/^2$. Because the complexes are electro-conducting materials, the hole-injection material poly(vinylcarbazole) (PVK; 0.025 M) was added to improve the balance of current carrier. Owing to the poor film-forming properties of the complexes, a very small quantity of poly (methylmethacrylate; PMMA; 0.001 M), which is inert to light and electricity, was used to improve the film-forming properties by mixing it with the organogallium complexes. A device structure of ITO–emissive layer–Al was employed. High-quality film can be obtained by spin-cast

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of PMMA, PVK and gallium complexes mixture dissolved in methylenechloride. An electron-injecting electrode Al was deposited on top by vacuum evaporation at pressure below 2×10^{-5} Torr with a deposition rate of 10–15 Å/s. The emitting area was $2 \times 3\ \text{mm}^2$. The luminance of the EL devices was measured with an AMINCO.BOWMAN luminance meter. All measurements were carried out at room temperature in air under DC bias conditions.

The current–voltage relationship of the EL device is shown in Fig. 3. The forward bias current can be obtained when the ITO electrode is positively biased and the Al electrode negatively. The current density increases when the forward bias voltage increases. The current density increasing rate is very low; it is from 0.18 to 2.25 mA/mm^2 for complex **1** and from 0.02 to 1.2 mA/mm^2 for complex **3** when the bias voltage increases from 1 to 13 V. The current density increasing rate for complex **1**, however, is higher than that of **3**.

The EL emission intensity–voltage relationships of the EL devices have been measured and are shown in Fig. 4. The light output of the EL diodes is proportional to the input voltage in the voltage range of 7–13 V (**1**) and 5–12 V (**3**).

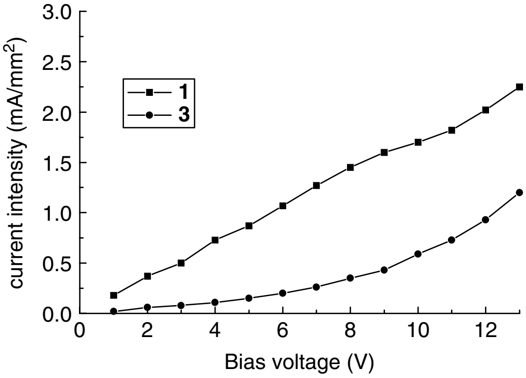

Figure 3. The relationship of current density and voltage of diodes with the emitter of **1** and **3**.

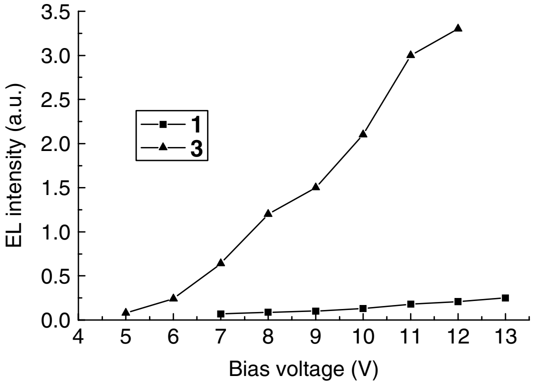

Figure 4. EL intensity–voltage curves of diodes with the emitter of **1** and **3**.

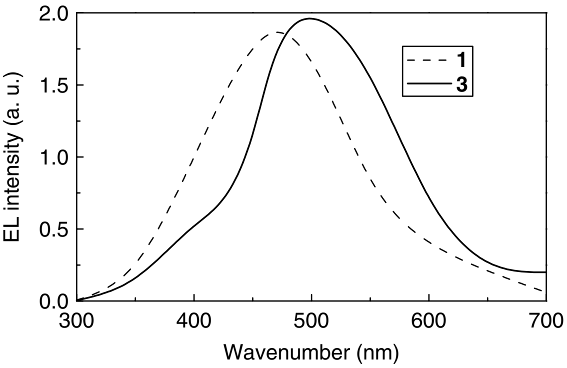

Figure 5. Electroluminescence spectra of complexes **1** and **3**.

The luminance increases with increasing forward bias voltage. The EL intensity increase rate of complex **3** is much larger than that of complex **1** when the voltage increases from 5 to 12 V. It may be attributed to the complex **3** of which the large delocalized conjugation system (anthryl) is presented. The driving voltages are 5 and 7 V, respectively, which are much lower than that of tri(1,3-diphenyl-1,3-propanediono)monophenathroline Eu(III) (25 V)[23] and similar to those of tris(8-hydroxyquinolinato)aluminum (below 10 V)[24] and dimethyl(*N*-arylmethylenethiobenzahydrazonato) gallium complexes.[19]

The EL luminescence spectra of the diodes are shown in Fig. 5. Their EL bands are located in the blue/green region. The EL emission maximums are 465 and 510 nm for complexes **1** and **3**, respectively. The EL luminescence maximums are related to the molecular structure. In view of effect of conjugate system on the EL emission band, conjugation of anthryl group with the large delocalized π-system is stronger than that of 2-methoxyphenyl group. The EL maximum for devices are at 465 nm (**1**) and 510 nm (**3**), a substantial red shift from those of PL [432 nm (**1**) and 479 nm (**3**); Fig. 5]. The possible cause of the red shift is the formation of the excitons between the PVK and the organogallium complex. Similar phenomena have been observed previously in EL devices using hole-injection material doped with organogallium complexes.[16,19,20] Complexes **1** and **3** have a similar structure but the emission energy of **1** has an approximately 45 nm blue shift relative to that of **3**. The large delocalized conjugation anthryl group in the ligand apparently increases the π^*–π energy gap, which is not surprising since the anthryl is more electronegative than the 4-methoxyphenyl, and thus capable of lowing the HOMO level and increasing the HOMO and LOMO gap. The EL spectrum is independent of the driving voltage and current, indicating that the radiative recombination of injected electrons and holes takes place in the gallium complexes. The role of gallium atom in the blue luminescence of complexes is therefore considered to be twofold. First, the formation of covalent bonds between the gallium and sulfur atom via the donation of long-pairs of nitrogen to gallium atom changes the emission energy.

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Second, the binding of thiobenzhydrozone ligands to gallium atom increase the rigidity of the ligands, thus reducing the loss of energy via vibration motions and increasing the emission efficiency.

SUMMARY

In summary, three diethylgallium complexes were synthesized and characterized. Monolayer light-emitting devices based on diethylgallium complexes doped poly(vinylcarbazole) were fabricated. The PL and EL properties were measured. The EL band is located in the blue/green region.

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