



## Photoluminescence and electroluminescence by gallium(III) complexes of N-salicylidene-o-aminophenol and its derivatives

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### ARTICLE INFO

#### Article history:

Received 16 May 2008

Received in revised form

15 December 2008

Accepted 18 December 2008

Available online 25 December 2008

#### Keywords:

N-salicylidene-o-aminophenol

Gallium complexes

Photoluminescence

Electroluminescence

Organic LED

### ABSTRACT

N-salicylidene-o-aminophenol and two of its derivatives bearing either an electron-donating methyl group or an electron-withdrawing Br group were used as ligands for the synthesis of three Ga(III) complexes. The complexes involved the participation of one acetylacetonate and one ethanol or methanol molecule. The geometry of the dianion of the Schiff base in the complexes is planar while photoluminescence data showed that photoluminescence intensity was extensively increased upon complex formation. Complexes emitted ligand-centered luminescence by ligand-centered excitation. Substituent groups broadly modified emission maximum. These substitutions can be exploited to tune light emission by the complex. All three complexes were used for the construction of electroluminescence devices and all emitted electroluminescence. Both photoluminescence and electroluminescence emission was enhanced in the case of substituted Schiff bases.

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### 1. Introduction

Small molecule organic light-emitting diodes (SMOLED) [1–4] are very interesting from many points of view: they are relatively easy to fabricate, reasonably stable and their active luminescent component is simple and rather easy to synthesize. Best-known among SMOLEDs are those based on Alq<sub>3</sub> (q = 8-hydroxyquinoline) [1,2,5]. Recent research on these metal-organic complexes, among other subjects, also focuses on the synthesis of Alq<sub>3</sub> variants. One possibility is to synthesize dinuclear complexes by adding a tridentate Schiff-base ligand: N-salicylidene-o-aminophenol (saphH<sub>2</sub>, see Fig. 1 for chemical structure), thereby increasing glass-transition temperature and improving stability of the emitting layer [6]. Another variant is to modify the emission wavelength by attaching an electron withdrawing chemical group (EWG) or an electron donating chemical group (EDG) [1,7–9]. Finally, a third variant is, of course, to change the complexed metal itself [6,10,11].

In the present work we focus on some of these possibilities with emphasis on the effect of substituent groups, either EWG or

EDG. For this purpose, we have synthesized chelates employing a single Schiff base, i.e. saphH<sub>2</sub>, thus simplifying the procedure. For the choice of metal we opted for Ga, since the obtained Ga–saph<sup>2-</sup> chelates were strongly photoluminescent, i.e. good candidates for SMOLED fabrication. Saph<sup>2-</sup> complexes with various metals, notably, Ga, Al and Be, are known for a long time and they have been used as fluorogenic reagents in various applications [8,9]. Fig. 2 shows the bonding mode of Ga to saph<sup>2-</sup>.

Bonds are formed with the two O atoms and N (tridentate ligand). Since the usual coordination number of Ga is 6, the complexes are formed by simultaneously complexing one molecule of the bidentate chelate acetylacetonate (acac<sup>-</sup>) and one molecule of ethanol (EtOH) or methanol (MeOH). An EtOH or a MeOH molecule was inevitably involved in the formation of the complex since these materials were used as solvents to synthesize the complexes. These chelates emit ligand-centered luminescence with ligand-centered excitation. The presence of the metal simply serves to stabilize ligand geometry. Indeed, since the intensity of fluorescence increases by metal complexation, without changing the spectral structure of the fluorescence spectrum, it is assumed that bonding with the metal, which inhibits rotation of the aminophenol vs. the salicylidene group, favors planarity and thus limits loss of excitation energy by internal conversion [12]. In addition, the planar geometry makes a more stable complex.

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This is the most plausible explanation of fluorescence enhancement by complexing group III metals [12]. In the present work, both photoluminescence (PL) and electroluminescence (EL) are studied by employing Ga(III) complexes based on  $\text{saph}^{2-}$  and two of its derivatives ( $5\text{Mesaph}^{2-}$  and  $5\text{Brsaph}^{2-}$ ). EL was studied using a standard device schematically shown in Fig. 3.

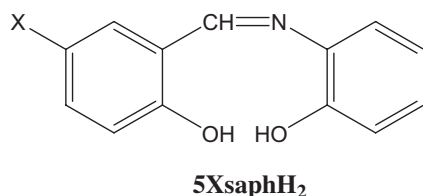
## 2. Experimental

### 2.1. Materials

Gallium (III) acetylacetonate [ $\text{Ga}(\text{acac})_3$ ], 2-aminophenol, 5-methylsalicylaldehyde (2-hydroxy-5-methyl-benzaldehyde) and coumarin-153 were obtained from Aldrich. 5-Bromosalicylaldehyde was from Fluka while salicylaldehyde and the rest of the reagents were from Merck. All chemicals were of the best quality available and were used as received.

### 2.1. Synthesis of *N*-salicylidene-*o*-aminophenol ( $\text{saphH}_2$ ) and its derivatives

Synthesis of  $\text{saphH}_2$  was made by the condensation in absolute ethanol of 2-aminophenol with salicylaldehyde in the case of unsubstituted Schiff base, or with 2-hydroxy-5-methyl-benzaldehyde, in the case of methyl-substituted Schiff base or with 5-bromosalicylaldehyde, in the case of bromo-substituted Schiff base, in accordance with literature methods [13]. The chemical structures of the free and substituted Schiff bases are shown in Fig. 1.



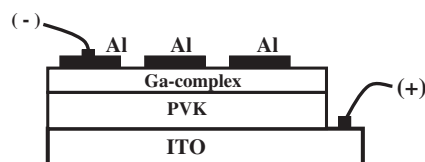
**Fig. 1.** Structure of the free ( $X = \text{H}$ ) and substituted ( $X = \text{CH}_3$ , or  $\text{Br}$ )  $\text{saphH}_2$  Schiff bases.

### 2.3. Synthesis of complexes bearing underivatized $\text{saphH}_2$ [ $\text{Ga}(\text{acac})(\text{saph})(\text{EtOH})$ ]

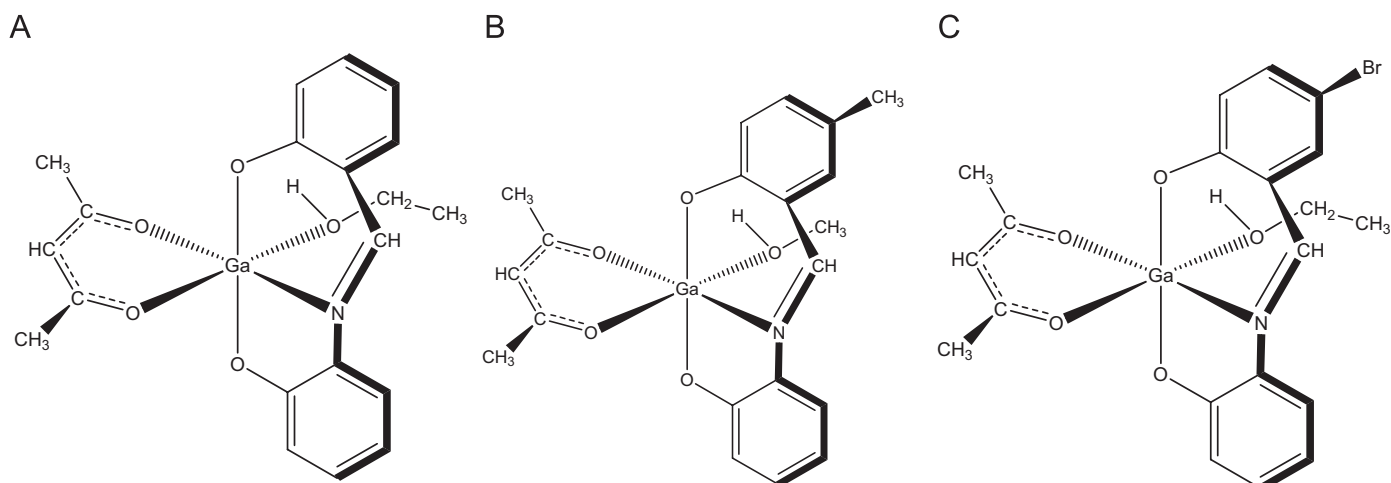
A yellow solution of  $\text{saphH}_2$  (0.021 g, 0.10 mmol) in EtOH (10 mL) was added to a colorless solution of [ $\text{Ga}(\text{acac})_3$ ] (0.037 g, 0.1 mmol) in the same solvent (10 mL). The clear yellow solution obtained was allowed to stand undisturbed for 1 day at room temperature. Two  $\text{acac}^-$  molecules are substituted by one  $\text{saph}^{2-}$  and one EtOH molecules in the complex. The hydroxyl hydrogens of the  $\text{saphH}_2$  are removed during the complexation process. Scheme 1 illustrates the complexation process while Fig. 2a shows the structure of the complex. Well-formed X-ray quality single crystals of [ $\text{Ga}(\text{acac})(\text{saph})(\text{EtOH})$ ] slowly appeared. The yellow crystals were isolated by vacuum filtration, washed with cold EtOH ( $2 \times 3 \text{ mL}$ ) and dried in air. The yield was 80% based on Ga. Anal. calcd. (%) for  $\text{C}_{20}\text{H}_{22}\text{GaNO}_5$  (Mr 426.15): C, 56.37; H, 5.20; N, 3.29. Found: C, 56.48; H, 5.17; N, 3.25. IR (KBr pellets,  $\text{cm}^{-1}$ ): 3440br, 3048w, 2968w, 2790w, 1620s, 1586s, 1546m, 1526s, 1474s, 1446w, 1386s, 1342w, 1308m, 1270m, 1222w, 1176m, 1154m, 1128w, 1090w, 1042m, 928m, 876w, 836m, 774w, 742m, 678w, 626w, 610w, 526w, 538m, 490w.

### 2.4. Synthesis of complexes bearing Me-derivatized $\text{saphH}_2$ [ $\text{Ga}(\text{acac})(5\text{Mesaph})(\text{MeOH})$ ]

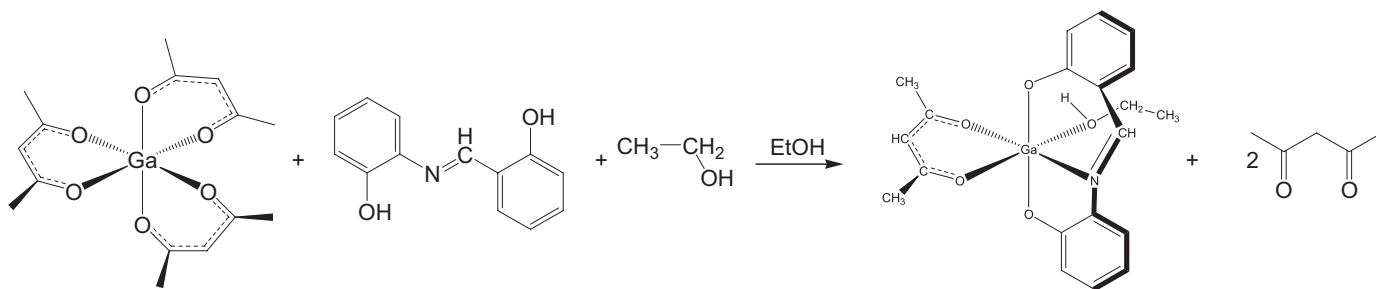
Solid [ $\text{Ga}(\text{acac})_3$ ] (0.037 g, 0.10 mmol) was added to a yellow-orange solution of Me-substituted  $\text{saphH}_2$  ( $5\text{MesaphH}_2$ ) (0.023 g, 0.10 mmol) in MeOH/EtOH (1:1 v/v, 20 mL). The yellow solution obtained was filtered and layered with  $\text{Et}_2\text{O}$ /hexane (1:1 v/v, 40 mL). Slow mixing yielded well-formed X-ray quality yellow crystals of [ $\text{Ga}(\text{acac})(5\text{Mesaph})(\text{MeOH})$ ]. Scheme 2 shows the process of this reaction while the structure of the complex is shown in Fig. 2b. The crystals were isolated by vacuum filtration,



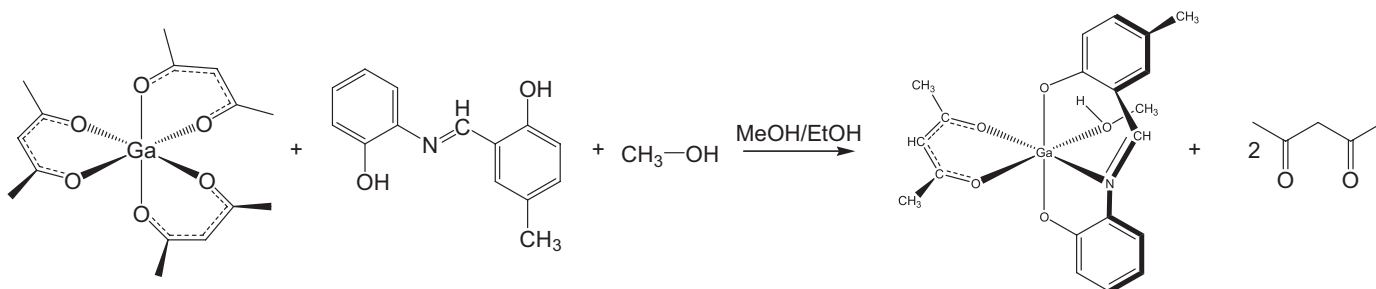
**Fig. 3.** Schematic representation of the SMOLED showing the layer by layer deposition.



**Fig. 2.** Structure and bonding in  $\text{Ga}(\text{acac})(\text{saph})(\text{Alcohol})$  complexes: (A) unsubstituted  $\text{saph}^{2-}$ ; (B)  $\text{saph}^{2-}$  derivatized with the EDG- $\text{CH}_3$  ( $5\text{Mesaph}^{2-}$ ) and (C)  $\text{saph}^{2-}$  derivatized with the EWG- $\text{Br}$  ( $5\text{Brsaph}^{2-}$ ).



**Scheme 1.** Reaction scheme for the formation of [Ga(acac)(saph)(EtOH)].



**Scheme 2.** Reaction scheme for the formation of [Ga(acac)(5Mesaph)(MeOH)].

washed with Et<sub>2</sub>O (2 × 3 mL) and dried in air. The yield was 78% based on Ga. Anal. calcd. (%) for C<sub>20</sub>H<sub>22</sub>GaNO<sub>5</sub> (Mr 426.15): C, 56.37; H, 5.20; N, 3.29. Found: C, 56.40; H, 5.14; N, 3.35. IR (KBr pellets, cm<sup>-1</sup>): 3003w, 2760w, 2552w, 1621m, 1588s, 1537s, 1478s, 1433w, 1393m, 1378s, 1315m, 1282m, 1270m, 1252w, 1214w, 1200w, 1161m, 1147w, 1134m, 1028m, 961w, 933w, 821w, 830m, 814w, 785w, 740m, 684w, 652w, 616w, 584w, 564w, 532w, 491w, 478w, 451w.

### 2.5. Synthesis of complexes bearing Br-derivatized saphH<sub>2</sub> [Ga(acac)(5Brsaph)(EtOH)]

A colorless solution of [Ga(acac)<sub>3</sub>] (0.037 g, 0.10 mmol) in EtOH (10 mL) was added to a yellow solution of Br-substituted saphH<sub>2</sub> (5BrsaphH<sub>2</sub>) (0.058 g, 0.20 mmol) in the same solvent (10 mL). The yellow solution obtained was filtered and allowed to stand undisturbed in the refrigerator for 13 days. Well-formed X-ray quality single crystals of [Ga(acac)(5Brsaph)(EtOH)] slowly appeared. The structure of this complex is shown in Fig. 2c. The yellow crystals were isolated by vacuum filtration, washed with Et<sub>2</sub>O (2 × 3 mL) and dried in air. The yield was 60% based on Ga. Anal. calcd. (%) for C<sub>20</sub>H<sub>21</sub>GaNO<sub>5</sub>Br (Mr 505.04): C, 47.56; H, 4.20; N, 2.77. Found: C, 47.69; H, 4.14; N, 2.82. IR (KBr pellets, cm<sup>-1</sup>): 3460br, 2348w, 2284br, 1658w, 1619s, 1610s, 1589m, 1524s, 1475s, 1458s, 1377s, 1307m, 1261m, 1248m, 1209w, 1169s, 1137w, 1114w, 1087w, 1045w, 875w, 826m, 744s, 678m, 648m, 620w, 580w, 544w, 518w, 493w.

### 2.6. SMOLED fabrication

SMOLEDs were fabricated in the standard configuration (see Fig. 3). Subsequent layers were deposited on indium tin oxide (ITO) glasses (Pilkington, about 10 Ω/square). First, poly(9-vinyl-carbazole) (PVK) was deposited by spin-coating at 3000 rpm using a 10mg/ml chloroform solution making a film of about 100 nm thick. On top of this layer, the active layer (Ga complex), of an approximate thickness of about 45 nm, was vacuum evaporated

(2 × 10<sup>-6</sup> mbar). Finally, a patterned Al electrode was also thermally evaporated to complete the cell. The cell was then sealed with epoxy resin under argon atmosphere, inside an Aldrich glove bag. The active area of the studied cells was 15 × 5 mm<sup>2</sup>.

### 2.7. Apparatus

I–V curves were recorded with a Thandar TS3021S DC power supply and a Keithley DMM-196 multimeter. Luminance was measured with a Minolta LS-110 luminance meter. UV–vis absorption measurements were made with a Cary 1E spectrophotometer. Photoluminescence of solutions of complexes in chloroform was recorded with a Cary Eclipse fluorometer. The photoluminescence quantum yields have been measured using coumarin-153 as a standard. Photoluminescence of thin films and electroluminescence spectra were recorded with an Ocean Optics S-2000 Diode Array spectrophotometer. Photoluminescence was excited by a 150 W xenon lamp. Crystallographic data sets were collected at 298 K using a P2<sub>1</sub> Nicolet diffractometer with Ni-filtered Cu-K<sub>α</sub> radiation (λ = 1.54180 Å).

## 3. Results and discussion

### 3.1. Molecular structure of the complexes

Complexes [Ga(acac)(saph)(EtOH)] and [Ga(acac)(5Mesaph)(MeOH)] were characterized by X-ray crystallography while preliminary X-ray characterization of complex [Ga(acac)(5Brsaph)(EtOH)] revealed that it is isostructural to [Ga(acac)(saph)(EtOH)]. Full crystallographic data and description of the molecular and crystal structures will be published elsewhere. In both complexes, the Ga<sup>III</sup> ion adopts a six coordinate distorted octahedral geometry with the alcohol oxygen and one of the acetylacetonate oxygen atoms to occupy the two axial positions. The 5Xsaph<sup>2-</sup> ligand chelates the Ga<sup>III</sup> ion through the imine

nitrogen atom and the deprotonated hydroxyl oxygen atoms all on the equatorial plane of the octahedron. One oxygen atom of the  $\text{acac}^-$  ligand is situated on the basal plane completing the octahedral environment around the metal centre. The crystallographic analysis revealed that both  $\text{saph}^{2-}$  and  $5\text{Mesaph}^{2-}$  dianions were planar within the complexes with an average deviation from the mean plane 0.031 and 0.063 Å (two independent molecules in the cell), in the case of  $\text{saph}^{2-}$  and 0.143 Å in the case of  $5\text{Mesaph}^{2-}$ . The crystal structure of the free ligand  $\text{saphH}_2$  contains two crystallographically independent molecules in the unit cell [14]. Both are planar with an average deviation from the mean plane of 0.081 and 0.109 Å. All three types of crystals can be sublimated by vacuum sublimation allowing to fabricate SMOLEDs.

### 3.2. Thermal stability of the complexes

The three complexes were synthesized by using ethanol or methanol as solvents. Inevitably, molecules of these small aliphatic alcohols were involved in the formation of the complexes, which were then vulnerable to alcohol evaporation at elevated temperature. For this reason, the stability of the complexes was tested by TGA. It has been found that all three complexes lose about 10% of their weight between 130 and 160 °C and they remain stable thereafter up to 250 °C. This 10% loss is associated with evaporation of alcohol molecules.

### 3.3. Photoluminescence measurements

Photoluminescence spectra of the three complexes can be obtained either in solution or in thin films. Complexes are soluble in chloroform. Fig. 4 shows absorption, excitation and emission spectra of free (i.e., uncomplexed) Schiff-base solutions in chloroform. All three types of spectra were modified by either methyl or Br substitution. The corresponding excitation and emission maxima are listed in Table 1. Absorption of unsubstituted  $\text{saphH}_2$  mainly occurs in the UV and secondarily in the near-UV while both substituted Schiff bases, i.e.  $5\text{MesaphH}_2$  and  $5\text{BrsaphH}_2$ , mainly absorb in the near-UV. The prevalent excitation mode for  $\text{saphH}_2$  and  $5\text{MesaphH}_2$  was also located in the near-UV (around 350 nm) but that of  $5\text{BrsaphH}_2$  was red-shifted by about 100 nm. Meanwhile, Curve #4 of Fig. 4C shows absorption spectrum of a concentrated solution of  $5\text{BrsaphH}_2$ . It is then seen that the corresponding absorption does have a small shoulder around 450 nm, which justifies the excitation mode for  $5\text{BrsaphH}_2$ . The emission maximum of the free Schiff base was red-shifted by substitution of either the EDG- $\text{CH}_3$  or the EWG-Br,

thus showing that both substitutions affect the electronic structure of the free base. However, the shift was much larger in the case of  $-\text{CH}_3$ .

As expected, the spectral profiles were extensively modified in going from the free Schiff bases to the Ga complexes. The corresponding data are found in Table 1 and Fig. 5. Both excitation and PL spectra were red-shifted with respect to the spectra recorded with uncomplexed Schiff bases. However, the emission maximum was still red-shifted in the case of the methyl substituted complex  $[\text{Ga}(\text{acac})(5\text{Mesaph})(\text{MeOH})]$  with respect to the unsubstituted complex  $[\text{Ga}(\text{acac})(\text{saph})(\text{EtOH})]$  but it appeared at a shorter wavelength in the case of the Br-substituted complex  $[\text{Ga}(\text{acac})(5\text{Brsaph})(\text{EtOH})]$ . PL of the complex can then also be modified by substitution. It is red-shifted in the case of an EDG substitution but appears at shorter wavelengths in the case of an EWG substitution. This finding is similar to that of Refs. [1,7] treating similar data referring to tris(5-aryl-8-hydroxyquinoline).

The most dramatic change in going from free to complexed Schiff bases was in the PL intensity. Indeed, complex formation resulted in an extensive increase of PL intensity, as it is obvious from the values of the photoluminescence quantum yields, listed

**Table 1**  
Photophysical data for free Schiff bases and complexes.

Sample	Excitation maximum (nm)	Emission maximum (nm)	Fluorescence quantum yield <sup>a</sup>
$\text{SaphH}_2/\text{chloroform}^b$	356	525	0.02
$5\text{MesaphH}_2/\text{chloroform}^b$	350	554	0.09
$5\text{BrsaphH}_2/\text{chloroform}^b$	454	536	0.06
Complex- $\text{Saph}^{2-}/\text{chloroform}^c$	460	534	0.29
Complex- $5\text{Mesaph}^{2-}/\text{chloroform}^c$	475	549	0.38
Complex- $5\text{Brsaph}^{2-}/\text{chloroform}^c$	426	525	0.39
Complex- $\text{Saph}^{2-}/\text{film}^d$	–	543	–
Complex- $5\text{Mesaph}^{2-}/\text{film}^d$	–	556	–
Complex- $5\text{Brsaph}^{2-}/\text{film}^d$	–	540	–
Complex- $\text{Saph}^{2-}/\text{EL}^e$	–	539	–
Complex- $5\text{Mesaph}^{2-}/\text{EL}^e$	–	562	–
Complex- $5\text{Brsaph}^{2-}/\text{EL}^e$	–	535	–

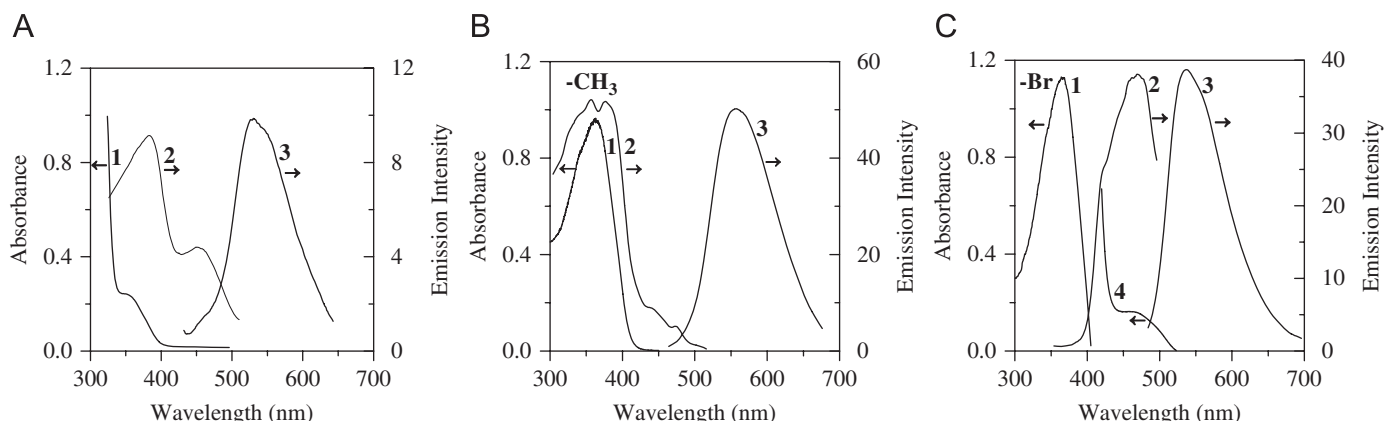
<sup>a</sup> Measured with coumarin-153 as a standard (quantum yield in ethanol 0.73 [15], in water 0.09 [15] and in chloroform 0.45).

<sup>b</sup> Free Schiff bases dissolved in chloroform (10 mg/L).

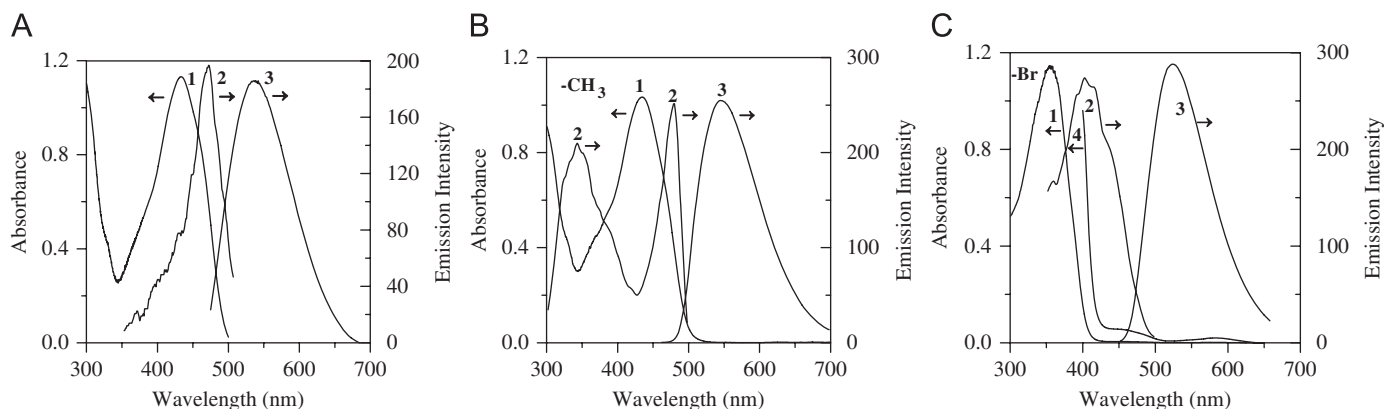
<sup>c</sup> Corresponding Ga complexes dissolved in chloroform (also 10 mg/L).

<sup>d</sup> Complexes cast as thin films on glass slides.

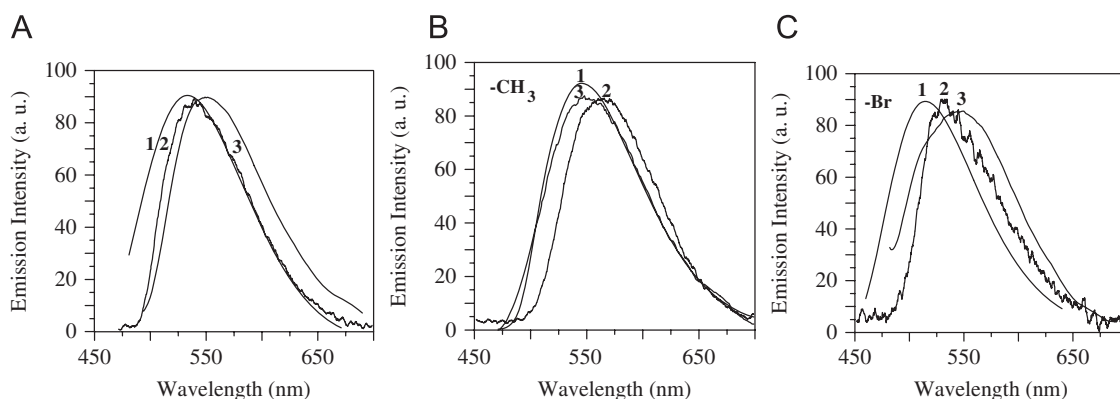
<sup>e</sup> Electroluminescence.



**Fig. 4.** Absorption (1); excitation (2) and emission (3) spectra of free Schiff bases in chloroform (10 mg/L): (A) unsubstituted  $\text{saphH}_2$ ; (B)  $\text{saphH}_2$  derivatized with  $-\text{CH}_3$  ( $5\text{MesaphH}_2$ ) and (C)  $\text{saphH}_2$  derivatized with  $-\text{Br}$  ( $5\text{BrsaphH}_2$ ). Curve C4 corresponds to the absorption spectrum of a concentrated solution in chloroform (100 mg/L). Each excitation spectrum was recorded at the emission maximum and each emission spectrum at the excitation maximum.



**Fig. 5.** Absorption (1); excitation (2) and emission (3) spectra of complexes in chloroform (10 mg/L). Complexes contained: (A) unsubstituted  $\text{saph}^{2-}$ ; (B)  $\text{saph}^{2-}$  derivatized with  $-\text{CH}_3$  ( $5\text{Mesaph}^{2-}$ ) and (c)  $\text{saph}^{2-}$  derivatized with  $-\text{Br}$  ( $5\text{Br saph}^{2-}$ ). Curve C4 corresponds to the absorption spectrum of a concentrated solution of the corresponding complex in chloroform (100 mg/L). Each excitation spectrum was recorded at the emission maximum and each emission spectrum at the excitation maximum.



**Fig. 6.** Comparison of the emission spectra of complexes in various environments: (1) photoluminescence of a  $\text{CHCl}_3$  solution (100 mg/L); (2) electroluminescence of a SMOLED and (3) photoluminescence of a thin film casted on a glass plate. The three complexes were based on: (A) unsubstituted  $\text{saph}^{2-}$ ; (B)  $\text{saph}^{2-}$  derivatized with  $-\text{CH}_3$  ( $5\text{Mesaph}^{2-}$ ) and (c)  $\text{saph}^{2-}$  derivatized with  $-\text{Br}$  ( $5\text{Br saph}^{2-}$ ).

in Table 1. As already discussed in Section 1, such a result was expected.

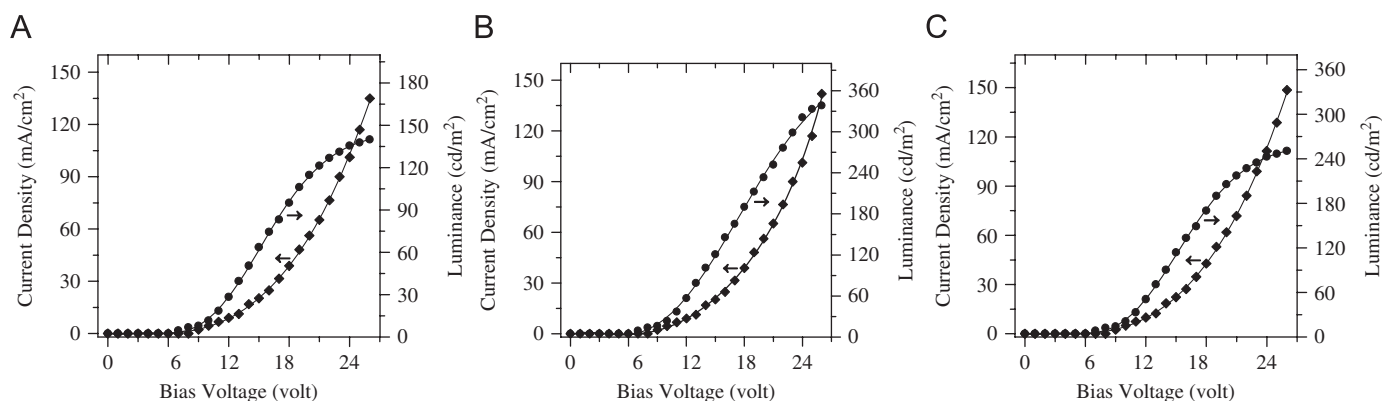
According to the crystallographic data, the Schiff bases are planar when they form a complex and for this reason their PL intensity increases (cf. Ref. [12]). Both excitation and PL spectra of these complexes seem to be affected by their environment on a molecular scale. It is unfortunate that the complexes are not soluble in a variety of solvents so as to investigate a solvatochromic effect. Nevertheless, when the complexes were cast as thin films their PL spectra were shifted again, as seen by the data of Table 1 and Fig. 6.

Even though the PL maxima in films were all red-shifted with respect to the corresponding spectra in solution, the PL maximum remained red shifted in the case of the methyl-substituted complex with respect to the unsubstituted complex but it appeared at a shorter wavelength in the case of the Br-substituted complex with respect to the unsubstituted complex. PL data then showed that an EDG or EWG substitution modifies the emission of Ga- $\text{saph}^{2-}$  complexes, indeed in different directions. As we already stated above, this was also detected with other complexes [1,7] but it may not always be the rule [16,17]. Such a diverse behavior should be expected. Careful examination of the above spectra reveals that their final appearance is a result of the extent of the red shift. Thus we may conceive blue shift in the case of the Br-substituted complex as a limited red shift with respect to the shift of the unsubstituted complex itself.

### 3.4. Electroluminescence

SMOLEDs were made with all three complexes and all produced EL. The EL spectra are shown in Fig. 6 and the EL maxima are listed in Table 1. The EL maxima did not coincide with the PL maxima of thin films. This may be due to the following three possible reasons: (1) The emission spectra of the present complexes, as already stated, seem to be very sensitive to the molecular environment, which is different in pure films and in EL devices. (2) Films prepared for electroluminescence were made by thermal evaporation under vacuum. This could lead to partial or total loss of alcohol molecules from the complexes, according to the data of Section 3.2. Loss of alcohol molecules justifies spectral modifications. Indeed, photoluminescence of films made by thermal evaporation does suffer a shift of PL maximum. (3) It is also possible that since electrons are exchanged between complexes and PVK, present in the EL devices, formation of exiplexes [18] might further influence spectral appearance. All these effects may also act simultaneously. However, we believe that loss of alcohol molecules is the main reason for the spectral modifications. In any case, the EL maximum was again red-shifted in the case of the methyl-substituted complex with respect to the unsubstituted complex but it appeared at a shorter wavelength in the case of the Br-substituted complex with respect to the unsubstituted complex. The present data show that it is possible to employ Ga complexes of the present structure to make





**Fig. 7.** IV and Luminance curves for SMOLEDs based on: (A) unsubstituted  $\text{saph}^{2-}$ ; (B)  $\text{saph}^{2-}$  derivatized with  $-\text{CH}_3$  ( $5\text{Mesaph}^{2-}$ ) and (C)  $\text{saph}^{2-}$  derivatized with  $-\text{Br}$  ( $5\text{Brsaph}^{2-}$ ).

SMOLEDs, which can offer EL in a large range of the visible spectrum. Work in progress in our laboratory studies substitution of  $\text{saphH}_2$  with other substituent groups hoping to cover an even larger spectral range.

Fig. 7 finally shows some additional data concerning SMOLED construction, i.e. voltage–current curves and luminance data. The threshold voltage was around 6 V in all three cases. Substituted  $\text{saph}^{2-}$  complexes gave higher luminance than the complexes of the unsubstituted Schiff base. This is in line with photoluminescence of free Schiff base (cf. Fig. 5). Obviously  $\text{acac}^-$  and alcohol molecules participating in the complex do not play any role in PL and EL but they come in only as complex stabilizing agents. This is expected, since  $\text{acac}^-$  is not fluorescent, while its absorption spectrum lies between 280 and 320 nm. Therefore, it is not excited under the present conditions and plays no role in the emission behavior of the complex.

#### 4. Conclusion

This work shows that complexes formed between  $\text{saph}^{2-}$  Schiff bases and Ga with  $\text{acac}^-$ , and alcohol acting as complex-stabilizing agents, can be used to fabricate SMOLED devices. Alcohol molecules may be lost during thermal evaporation but this does not affect functioning of the complexes as emitting layer in the construction of SMOLEDs. When a complex is formed, crystallographic data show that the geometry of the ligand is planar while PL data show a dramatic enhancement of the emission intensity. Methyl (EDG) or Br (EWG) substitution in  $\text{saph}^{2-}$  shifts the EL emission to larger or smaller wavelength, respectively, while both PL and EL intensities are enhanced by substitution.

#### Acknowledgements

A.K. and Th.F.Z. wish to thank the Research Committee of the University of Patras (K.KARATHEODORY Program) for financial support of this work while V.B. and P.L. acknowledge financial support from the program of Bilateral R&T cooperation between Greece and Cyprus of the Greek General Secretariat of Research and Technology.

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