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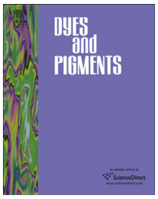

Synthesis and photophysical characterization of organotin compounds derived from Schiff bases for organic light emitting diodes

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ABSTRACT

The multicomponent reaction of the 2-hydroxynaphthaldehyde with 2-aminophenol derivatives and their *in situ* complexation with diphenyltin oxide in acetonitrile provided, in high yield, the products: (((*E*)-12-nitro-8,8-diphenylbenzo[*d*]naphtho[1,2-*h*][1,3,6,2]dioxazastannonine and (*E*)-11-nitro-8,8-diphenylbenzo[*d*]naphtho[1,2-*h*][1,3,6,2]dioxazastannonine), where tin atom is pentacoordinated. The synthesis of their ligands ((*E*)-1-(((2-hydroxy-5-nitrophenyl)imino)methyl)naphthalen-2-ol and (*E*)-1-(((2-hydroxy-4-nitrophenyl)imino)methyl)naphthalen-2-ol) is also reported. The chemical structure of all the compounds has been established by nuclear magnetic resonance (^{1}H, ^{13}C, and ^{119}Sn), infrared spectroscopy, and high resolution mass spectrometry. The 12-nitroanalogue was characterized by single-crystal X-ray structural analysis. The structure indicates that the backbone is essentially planar and the metal center resides in trigonal bipyramid geometry. The photophysical properties of the imines and those of the tin complexes were determined in solution exhibiting quantum yields around 4% with lifetimes in the range 10^{-10}–10^{-11} s. In a preliminary study, a diode was fabricated by a spun film of the 12-nitroanalogue, the device showed intrinsic electroluminescence properties with a threshold voltage at 13 V, a high current density (500 mA/cm^2) but a low luminance (0.03 cd/m^2).

1. Introduction

Since the first luminescent metal organic complex of 8-hydroxyquinoline aluminum (Alq3) was reported as an emitter material in organic light emitting diodes (OLEDs), tremendous progress has been made in this field due to potential applications in flat panel displays [1]. In this regard, much attention has been paid to transition metal complexes due to their interesting electroluminescent properties (highly emissive, good thermal stability) [2]. However, heavy metals such as Ir [3], Pt [4], and Cu [5] are extremely moisture- and/or oxygen-sensitive.

Among the main group of organometallic compounds, organotin materials have received considerable attention in recent years because of their commercial and biomedical applications [6]. It has been reported that several organotin complexes are effective fungicides, anti-fouling, pesticides [7], bactericides [8] and antitumor agents [9]; they are active catalysts and can also be used as reagents in organic reactions [10]. In particular, the attention has increased to those organotin complexes derived from Schiff bases, because they provide an interesting and wide variety of molecular structural conformations and in addition the electron withdrawing −C=N- group interacts with metal ions giving push−pull complexes with different optoelectronic properties [11] with potential applications [12]. Recently, it has been reported that organotin compounds derived from Schiff bases present thermochromism but fluorescence properties were not described in order to understand this property [13]. Tao et al. report the synthesis of a green emitting tetravalent tin complex (Scheme 1) with high electron affinity that has been used as an active electroluminescent layer in organic light emitting diodes (OLEDs) [14]. It should be noted that OLEDs with these small molecules are successfully fabricated only by thermal evaporation, but not by spin-coating process, which is a more economic and versatile deposition technique [15]. Therefore, the challenge is to find materials that form homogeneous spun films with high quantum yields.

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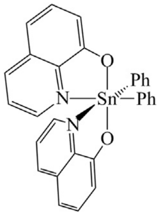


Scheme 1. Organotin complex applied in OLED preparation.

We have been interested in the synthesis, characterization [16], biological [17], and catalytic activity [18] of organotin complexes derived from ligands with donor atoms. Here we report the synthesis and photoluminescent properties of two new organotin complexes **3** and **4** derived from tridentate ligands 1 and 2 (Scheme 2). The X-ray single-crystal structure (**3**), thermal and photophysical properties of the compounds have been investigated. To demonstrate their potential application in an organic electroluminescent diode, a preliminary study on the electroluminescent properties of **3** is reported. Both, organic and organotin compounds were fully characterized by NMR (^{1}H, ^{13}C, and ^{119}Sn), UV–vis, IR spectroscopy, mass and fluorescence spectroscopy.

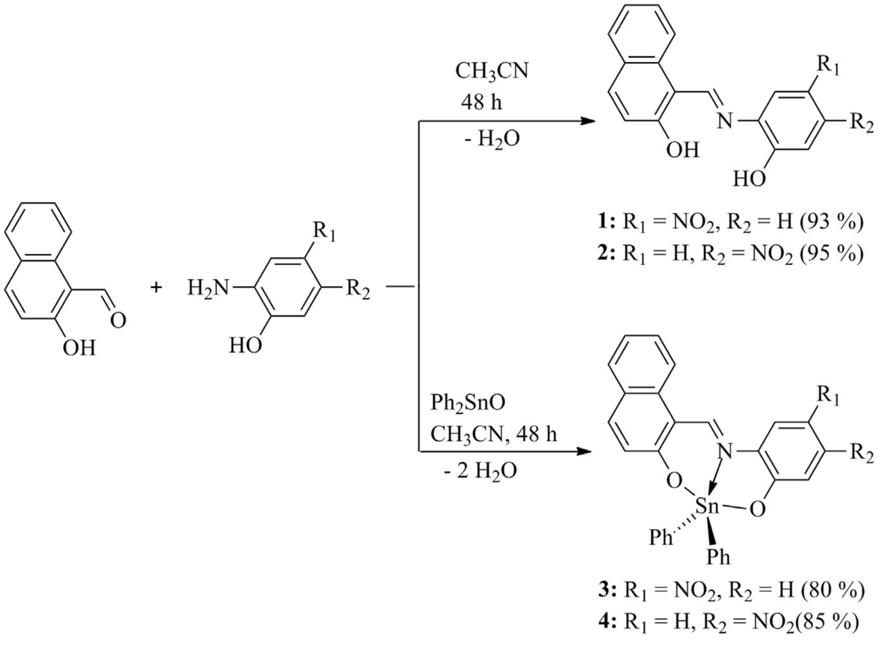
2. Results and discussion

2.1. Syntheses

The multicomponent reaction composed by 2-hydroxynaphthal dehyde, aminophenol derivate and diphenyltin oxide in a 1:1:1 M ratio (Scheme 2) provided the new pentacoordinate tin compounds (**3**: (*E*)-12-nitro-8,8-diphenylbenzo[*d*]naphtho[1,2-*h*][1,3,6,2]dioxazastannonine and **4**: (*E*)-11-nitro-8,8-diphenylbenzo[*d*]naphtho[1,2-*h*][1,3,6,2]dioxazastannonine) in good yields. In order to carry out a comparative study of the optoelectronic properties, the homologs tin free Schiff bases (**1**: (*E*)-1-(((2-hydroxy-5-nitrophenyl)imino)methyl) naphthalen-2-ol and **2**: (*E*)-1-(((2-hydroxy-4-nitrophenyl)imino) methyl)naphthalen-2-ol) were also synthesized. All the compounds were recrystallized from dichloromethane/hexane (2:8) solution; it is noteworthy that only compound **3** formed good quality monocrystal that could be structurally characterized by single X-ray diffraction. All the compounds are soluble in common organic solvents such as ether, chloroform, THF and ethyl acetate.

2.2. Spectroscopic characterization

The ^{1}H NMR spectra of compounds **3** and **4** exhibit one signal at 9.58 and 9.56 ppm with coupling constants $^{3}J(^{1}H,^{119}Sn)$ of 60 and 59 Hz, respectively, which are indicative of the new N=C bond formation and of the N → Sn coordination. The ^{1}H signals of the H-*ortho* [$^{3}J(^{1}H,^{119}Sn) = 85$ Hz] from the Ph_2Sn moiety show a deshielding effect due to their intramolecular interaction with the oxygen atoms which were corroborated by X-ray diffraction analysis, *vide infra* (C(25)-H*o*•••O(2) 2.547(3) Å; ∠ C–H•••O 120.81°, C(29)-H*o*•••O(1) 2.554(3) Å; ∠ C–H•••O 113.52°), and meaning that phenyl groups substituted on the Sn atom are stable in solution [19]. For the unambiguous assignment of the proton and carbon resonant signals, it was essential to make HETCOR and COSY experiments (see Electronic Supplementary Material). The ^{13}C NMR data are given in Table 1. The aromatic resonances of the diphenyltin complexes **3** and **4** are assigned on the basis of both, aromatic $^{n}J(^{13}C–^{119/117}Sn)$ coupling constants and signal intensities. Compounds **3** and **4** exhibit a $^{1}J(^{13}C–^{119}Sn)$ of 1124 and 1032 Hz, respectively. The relationship between bond angles C–Sn–C and the magnitude of $^{1}J(^{119}Sn, ^{13}C)$ [20] predicted for the C–Sn–C angle for 3 as 127.75° (between extremes of 119.2 and 143.4°), which is almost the same with the experimental value C(18)–Sn–C(24) 127.76(19)° suggesting that the tin atom has a slightly distorted trigonal bipyramid geometry. The C-*ipso*, C-*ortho*, C-*meta*, and C-*para*, from Ph_2Sn, were unambiguously assigned by their corresponding $^{n}J(^{119}Sn, ^{13}C)$ values. The ^{119}Sn NMR spectra of the complexes **3** and **4** in $CDCl_3$ solution exhibit a single resonance signal in the characteristic range for five-coordinated compounds (**3:** – 317.8, **4:** – 317.5 ppm) [21]. The five-coordinated diphenyltin structure for complex **3** is evidenced by X-ray diffraction. IR spectral analysis showed stretching bands at 1539 and 1537 cm^{-1} which



Scheme 2. Synthesis of Schiff bases ligands (**1** and **2**) and their tin complexes (**3** and **4**).