Organic Electronics xxx (2012) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Synthesis and luminescence properties of lithium, zinc and scandium 1-(2-pyridyl)naphtholates

Mikhail E. Burin [a,*], Vasily A. Ilichev [a], Anatoly P. Pushkarev [a], Dmitry L. Vorozhtsov [a], Sergey Yu. Ketkov [a], Georgy K. Fukin [a], Mikhail A. Lopatin [a], Alexander A. Nekrasov [b], Mikhail N. Bochkarev [a]

[a] G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Tropinina str. 49, 603950 Nizhny Novgorod, Russia
[b] A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky Prospect 31, 119071 Moscow, Russia

ARTICLE INFO

Article history:
Received 29 May 2012
Received in revised form 25 September 2012
Accepted 27 September 2012
Available online xxxx

Keywords:
Electroluminescence
Non-doped OLED
Lithium
Zinc
Scandium
Pyridylphenolate

ABSTRACT

1-(2-Pyridyl)naphth-2-ol (pynH) was synthesized from 2-bromopyridine and 1-bromo-2-hydroxynaphthalene and structurally characterized. This ligand and the known 2-(2-pyridyl)phenol (ppH) ligand were reacted with $LiN(SiMe_3)_2$, $ZnEt_2$ and $Sc[N(SiMe_3)_2]_3$ to prepare the new luminescent complexes Li(pp), Li(pyn), $Zn(pyn)_2$, $Sc(pp)_3$, $Sc(pyn)_3$ and known $Zn(pp)_2$. Photoluminescent (PL) spectra of the compounds contained a single broad band with a maximum at 447–473 nm. The OLED devices with a configuration of ITO/TPD/complex/Bath/Yb gave blue–green emission. The emission spectra of these devices resembled the PL spectra; however, the bands of electroluminescence (EL) were shifted 20–40 nm to the long-wavelength side. A maximum current efficiency 15.3 cd/A and a power efficiency 8.12 lm/W at 100 cd/m^2 were measured for the device with the zinc luminophore $Zn(pp)_2$, whereas the highest luminance of 8300 cd/m^2 at 22.5 V was observed with the device with the scandium complex $Sc(pp)_3$. DFT calculations showed that the latter complex exhibited the lowest HOMO and the highest LUMO energy levels compared with the other investigated compounds. The calculated trends with respect to the influence of the metal and the ligand on the LUMO–HOMO gap agree well with the shifts of the electronic transitions observed in the PL spectra of the complexes.

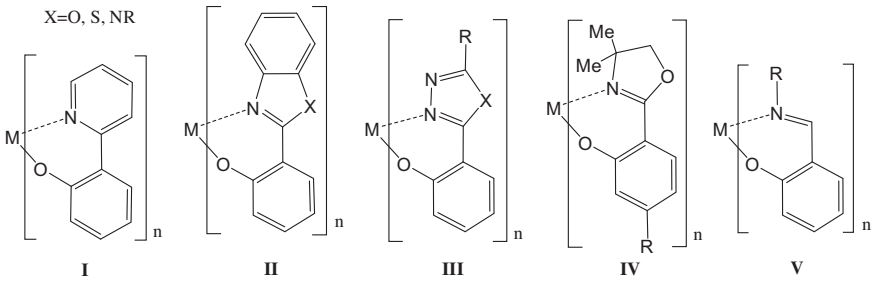
1. Introduction

In addition to 8-hydroxyquinolates, the main type of anionic ligands in nontransition-metal metallocomplexes designed for OLEDs is phenolates that contain N-heterocyclic substituents (**I**, **II**, **III**, **IV**) or amido groups (**V**) at the 2-position.

In all these complexes, ligands bound to the metal center through the chelate –OCCCN– fragment form stable 6-membered metallocycles. Because of this structure, the metal atom is associated with the system of conjugated π-bonds of the ligands, which is necessary for the luminescence of the metallocomplexes. Compounds of this type with Li, Be, B, Zn, Sc or Pt are used as emitters in OLED devices [1–6]. Notably, the same structural motif is present in the molecules of the most famous electroluminophore, tris(8-hydroxyquinolate)aluminum (Alq_3) [7], and in 8-hydroxyquinolates of other nontransition [4b,8] and rare-earth metals [9]. The second distinctive feature of complexes **I**, **II**, **III**, **IV** and **V** (besides their metallocycle structure) is the presence of phenolate fragments, RC_6H_4–O–M. According to density functional theory calculations on these complexes, the highest occupied molecular orbital (HOMO) is located largely on the phenoxide, and the lowest unoccupied molecular orbital (LUMO) mainly distributes on the phenoxide and N-heterocycles. The width of the HOMO–LUMO energy gap in these complexes varies from

* Corresponding author. Tel.: +7 831 435 40 21; fax: +7 831 462 74 97.
E-mail addresses: burin@iomc.ras.ru (M.E. Burin), secp@elchem.ac.ru (A.A. Nekrasov).

1566-1199/$ - see front matter © 2012 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.orgel.2012.09.021



1.9 to 4.1 eV, depending on the nature of the substituent X in the XC_6H_4 ring. Accordingly, the emission color of the complexes can be tuned from deep blue to green, yellow and red by changing the substituents. The same design strategy is used to increase the EL efficiency of the compounds. The effects of changes in the phenolate fragments on the luminescent characteristics of compounds have been studied less frequently. A rare example of such a study is the work of Sano et al. [4b], who showed that the change of electron-donating substituents *R* with electron-withdrawing groups in the zinc derivatives of type-**IV** complexes leads to a decrease of the HOMO level, a shift of the emission band to the blue region and an increase in the quantum yield of luminescence. To study the dependence of the luminescent properties of the metallocomplexes on the nature of the O,N-chelated aromatic ligands, we synthesized 2-(2-pyridyl)phenol, 1-(2-pyridyl)naphth-2-ol and their complexes with Li, Zn and Sc. The investigation of the PL and EL of the obtained compounds showed that the replacement of phenol with naphthol groups in the ligands causes a minor change in the luminescent efficiency. The luminescent characteristics of the devices depend to a significantly greater extent on the nature of the metal in the complexes. Notably, replacing phenylpyridyl ligands with naphthylpyridyl in iridium complexes resulted in an efficient clear-yellow phosphore [10].

2. Results and discussion

2.1. Synthesis of the ligands and metallocomplexes

1-(2-Pyridyl)naphth-2-ol (pynH) was synthesized via the Kumada coupling of 2-methoxy-1-bromonaphthalene with 2-bromopyridine catalyzed by palladium phosphine followed by demethylation with HCl, according to the modified procedure shown in Scheme 1 [11].

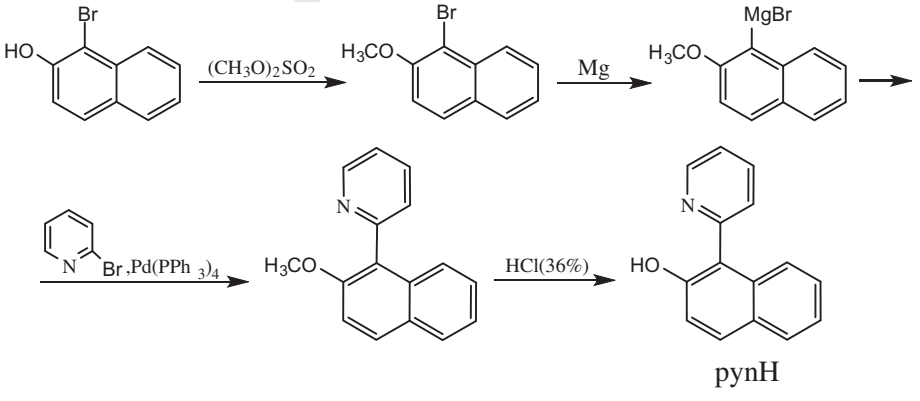
The product was isolated as a colorless microcrystalline solid with m.p. 125 °C. 2-(2-Pyridyl)phenol (ppH) was prepared from 2-bromophenol and 2-bromopyridine according to the method reported in the literature [11].

Both ligands were used in the reactions with lithium silylamide, diethylzinc and scandium silylamide, according to Scheme 2 for the preparation of novel (except $Zn(pp)_2$) chelate complexes of these metals.

All of the reactions proceeded under mild conditions and afforded the desired products in 84–98% yield. The complexes were isolated as pale-yellow powders that were stable in air, sparingly soluble in THF and sublimable under high vacuum without decomposition; when heated to temperatures greater than 270 °C in sealed capillary tubes, the compounds decomposed without melting. The identity of the obtained complexes was confirmed by infra-red spectroscopy (IR), elemental analysis and mass spectrometry. Complex $Zn(pp)_2$ was identified by comparison of its characteristics with those reported previously [4c].

2.2. Structure and computation

The X-ray analysis showed that, in a molecule of pynH (Fig. 1), the relative positions of the planes of the pyridyl and naphthyl fragments are close to orthogonal (the dihedral angle is 84.23°), unlike the case of 2-(2-pyridyl)phenol (ppH), where the pyridyl and phenyl rings are almost coplanar (the dihedral angle is 8.7(2)°) [11]. The bond lengths and angles in pynH are typical of such compounds (Table 1). In a crystal, the pynH molecules form zigzag



Scheme 1. The synthetic route for the ligand pynH.

Please cite this article in press as: M.E. Burin et al., Synthesis and luminescence properties of lithium, zinc and scandium 1-(2-pyridyl)naphtholates, Org. Electron. (2012), http://dx.doi.org/10.1016/j.orgel.2012.09.021