



New class of easily-synthesizable and modifiable organic materials for applications in luminescent devices



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ARTICLE INFO

Article history:

Received 9 August 2016

Received in revised form

19 November 2016

Accepted 20 November 2016

Available online 24 November 2016

Keywords:

OLEDs

Boronic acids

8-Hydroxyquinoline

Luminescence

Time-resolved spectroscopy

ABSTRACT

New class of cheap, easily-synthesizable and modifiable organic luminescent materials is presented. 1,2-phenylenediboronic acid reacts with 8-hydroxyquinoline in high yield, both in solution and under mechanochemical conditions, and forms a brightly luminescent complex (emission maxima *c.a.* 500 nm (solid state) – 525 nm (solution)). This very first luminescent boronic 8-oxoquinoline complex exhibits emission lifetime of ns order, which, together with the DFT results, indicates a singlet-singlet origin of the fluorescence. The emission quantum yield, determined in acetonitrile is significant (*c.a.* 15%) and may be increased by choice of solvent. Additionally, the impact of the enhanced Lewis acidity of boron centres in the acid moiety was investigated on a series of the fluoro derivatives of 1,2-phenylenediboronic acid reacted with 8-hydroxyquinoline. In general, the *mono*-oxyquinolinato complex is preferably formed, however, in the case of the *tetra*-fluorinated acid a doubly-coordinated complex is stable and favourable. Interestingly, all of the fluorinated complexes exhibit highly comparable luminescent properties to the parent complex. Importantly, the obtained complexes appeared to be electroluminescent, thus a working OLED was successfully produced and tested.

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1. Introduction

Many efforts are put nowadays into finding new cheap functional materials of desired properties, with great emphasis on photoactive substances applicable as sensors, biomarkers, optoelectronic devices, *etc.* [1] Especially interesting here are coordination compounds. Many of these, however, require rather rare and expensive metal centres, such as, Ir, Rh or Ru. Thus, alternative materials based on more common and cheaper elements are being actively sought and tested. These include organic systems, such as boron-containing species. First promising compounds of this kind for applications in photo- and electroluminescent devices were reported in late 90's [2]. The prototype complexes obtained by Anderson et al. [3] were based on 8-oxyquinolinato ligand (Q)

bound to the boron centre, similarly as it is found in the aluminium tris(quinolin-8-olate) (AlQ₃) complex known for its strong green electroluminescent properties [4]. Since then, many complexes were synthesized and comprehensively characterized, among which the studied by us low-cost luminescent *boronic*-type complexes (R₂BQ) [3,5], as well as the 9,10-dihydro-9,10-diboraanthracene based systems [6]. In contrary, more accessible and more stable *boronic acid* (RB(OH)₂) derivatives were known to be neutral versus 8-hydroxyquinoline, and thus no luminescent complexes of that kind were reported to date. Instead, they constitute excellent building blocks for crystal engineering and supramolecular chemistry purposes. Consequently, a great number of various co-crystals have been obtained with either *mono*-boronic acid species [7], or *meta*- [8] and *para*-phenylenediboronic acids [7a,9].

Natural extension of the above-mentioned investigations concerned the application of *ortho*-phenylenediboronic acid (**odba**) [10]. It appeared that a simple one-pot 1:1 reaction of the **odba** acid

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with 8-hydroxyquinoline (**8-HQ**) provides new photoactive species (Scheme 1, Fig. 1). The reaction proceeds in high yield in common organic solvents (acetone, acetonitrile, tetrahydrofuran, 1,4-dioxane, dichloromethane, etc.) at ambient conditions, and results in a yellow solution of the final complex (**1**, Scheme 1, Fig. 1a). In turn, the solvent evaporation yields high quality yellowish crystals suitable for X-ray diffraction structure determination (Fig. 1b).

Hence, here we report crystal structures and spectroscopic properties of the representative compounds of this new class of promising easily-synthesizable and modifiable luminescent organic materials. Our studies are supplemented by analysis of fluorinated derivatives of the complex **1** (Scheme 1), so as to investigate the impact of boron-centre acidity modifications on the examined properties. Additionally, the performance of the fabricated organic light emitting diode (OLED) based on the synthesized complexes is presented.

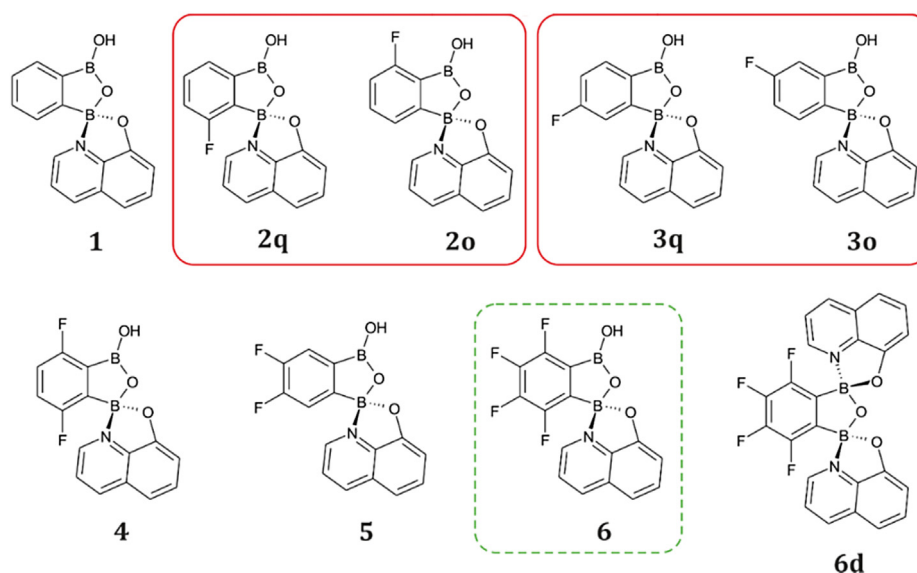
2. Results and discussion

2.1. Synthesis and solution equilibria

The parent *ortho*-phenylenediboronic acid can exist in the solution in the acidic (form **a**, Scheme 2) or the cyclic semianhydride

form (form **b**), as has been earlier reported by us [10]. Form **b** appears to be responsible for the efficient formation of the studied complex in solution. In order to further explore the solution equilibria, a series of **odba** derivatives with various number and location of fluorine substituents, which affects Lewis acidity of boron centres, was reacted with 8-hydroxyquinoline, according to Scheme 1. Every acid was treated with an equimolar amount of **8-HQ**, which resulted in the formation of the type **I** complex, whereas in the excess of **8-HQ** the type **II** products were observed in different relative quantities, depending on the acid used.

The increased number of fluorine atoms attached to the aromatic ring generally enhances the acidity of boron centres, which results in greater coordination capabilities towards the **8-HQ** moiety. In the case of the parent **odba**, the *mono*-substituted complex **1** is favoured, however, for the fluorinated acids the addition of excess amount of **8-HQ** resulted in the formation of equilibrium between forms **I** and **II**. Furthermore, the nuclear magnetic resonance (NMR) spectroscopic studies (^1H , ^{19}F and ^{11}B NMR spectra of compounds dissolved in wet CDCl_3) indicate that this equilibrium is very sensitive to the water content in the examined solution. Finally, in the case of the *tetra*-F-substituted **odba**, the doubly-8-oxyquinolinato-complex **6d** constitutes the preferred product. Fig. 2a-d below illustrates the spectroscopic



Scheme 1. Schematic representation of the studied complexes. Abbreviations for complexes **2** and **3** indicate the position of the fluorine atom (**q** – at the side of the **Q** ligand, **o** – at the OH group side); abbreviation for complex **6d** indicates the double 8-oxyquinolinato substitution (**d** – double). Both forms of **2** and **3** co-exist in solution and in the solid state (as depicted in rounded solid-line rectangles; see text for explanation). Complex **6** was not isolated independently (rounded dashed-line rectangle).

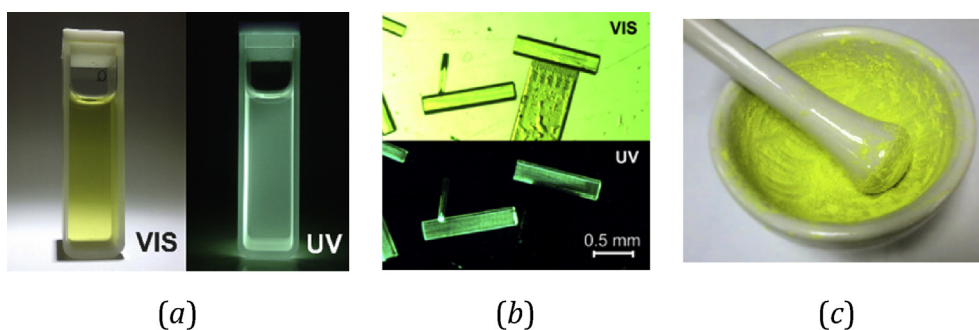


Fig. 1. Compound **1** in acetone solution (a) and as single crystals (b) shown in natural light (VIS) and in dark when irradiated with UV light (UV). (c) Complex **1** obtained in the mechanochemical reaction.

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