



Luminescent benzo- and naphthoquinolines: Synthesis and investigation of photophysical properties



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ABSTRACT

The aim of this study was to synthesise new luminescent small molecular weight benzo- and naphthoquinoline derivatives (based on already known synthons) with different substituents (chlorine, tetrazole, iminophosphorane and amine), to characterize them by ultraviolet photoelectron spectroscopy in air (UPS), luminescence and absorption photospectrometry and to investigate the changes in these properties resulted by differences of molecular structure. Measured values of the HOMO, the LUMO energy levels and optical band gap ($E_{g,opt}$) were in range $E_{HOMO} = [-5, 9; -5, 5]$ eV, $E_{LUMO} = [-3, 6; -3]$ eV, $E_{g,opt} = [2; 2, 8]$ eV. Most of the examined materials showed high intensity fluorescence reaching quantum yields of 49%. Fluorescence peaks of thermally evaporated layers distributed in range of $\lambda_{Layer} = [477; 596]$ nm – from blue to orange colour while in chloroform solution remained in blue-green interval $\lambda_{Solution} = [471; 537]$ nm. Primary study results of electroluminescence indicate that the materials have a potential to be used in organic optoelectronics.

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1. Introduction

Small organic molecules with a conjugated π -electron system usually exhibit semiconducting behaviour. Hence, they are potential materials for electronic and optoelectronic devices, such as organic field effect transistors (OFETs) [1,2], organic photovoltaic cells (OPVCs) [3] and organic light emitting diodes (OLEDs) [4]. Also, high degree of π -conjugation usually exposes unique fluorescent properties in a solution and solid state. A colour of emission depends upon the size of the HOMO–LUMO energy gap, which for visible light (380–780 nm) corresponds to 1.5–3.2 eV [5]. However, synthesis of molecules obtaining eligible structure and photophysical properties required for these devices is challenging. Therefore, it is an obligation of chemists and physicists to unite for this highly meaningful research work.

Quinoline derivatives have been synthesized intensively for their bioactivity and relevance to medical treatment [6–9]. However, besides pharmaceutical applications they are also suitable as fluorescent dyes or as emissive and charge transport layers in OLED structures [10]. First fluorescence measurements of quinoline based materials were performed more than 70 years ago [11]

and these researches are further being carried extensively. Our benzo- and naphthoquinoline derivatives are valuable starting materials for a wide variety of N-heterocyclic compounds used in optoelectronic devices.

Herein, we report a convenient synthesis and investigation of photophysical properties of small molecular weight benzo- and naphthoquinoline derivatives having varied substituents (chlorine, tetrazole, iminophosphorane and amino groups). Synthesis of some materials (2a, 3a, 4a, 5a and 5g) has been already described publicly [7,12–14,29] yet the significance of our study is that we compare photophysical properties of solution and thin-film of newly synthesized molecules with their already mentioned analogues. This allows us to present not only complex information about detailed process of synthesis, but also some insights regarding molecular structure influence on photophysical material properties.

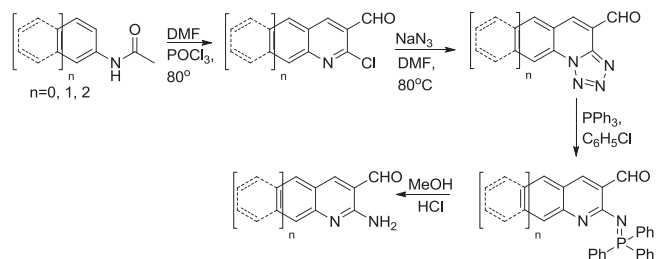
2. Synthesis of quinoline derivatives

Different investigated derivatives of quinoline were synthesized in the same manner (Scheme 1) [12].

The primary aryl amines were taken as starting compounds and their acetylation occurred by the treatment with an acetic anhydride. The key step in the preparation of the target

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Scheme 1. Synthesis of quinoline derivatives.

compounds was synthesis of 2-chloro-3-carbaldehydes. The resulting aryl acetamides were further cyclized by the treatment with the Vilsmeier–Haack reagent (DMF+POCl₃) [13].

The next step of this method was replacement of chlorine group with sodium azide in DMF (Scheme 1). It was found that the reaction time of investigated *o*-chloroquinolines was different (6–24 h). It was observed that smaller molecules react much faster. All synthesized products had poor solubility in different solvents. They were isolated in good yields (82–94%). All products exist in tetrazole tautomer as described in Ref. [14].

The obtained tetrazole ring containing derivatives were treated with PPh₃ in chlorobenzene. The products were isolated in good yields (68–96%). Then we compared the ¹H NMR spectrum data of different tetrazoles. Protons of the aldehydes appeared in the most downfield region (from 10,95 ppm and more).

The last step of this useful method was acid hydrolysis of iminophosphoranes in HCl/MeOH solution. The *o*-aminoaldehydes were isolated in good yields (64–84%). All structures of compounds were assigned according to spectral and elemental analysis.

This method is appropriate to synthesize larger quantities (up to 5 g) and to prepare compounds having two or three aromatic

rings.

3. Measurements of values of the HOMO and the LUMO energy levels

Primarily we had an interest to measure values of energy levels of HOMO, LUMO and optical band gap energy ($E_{g, opt}$) according to their relevance to the device design [15]. Values of the HOMO energy level were obtained by UV photoelectron spectroscopy in an air method [16] described in instrumentation section (Supplementary information part). This method allows us to determine the minimum amount of energy needed to tear a single electron loose (and move to infinity) under illumination – in other words, approximated ionisation energy or the HOMO energy level for organic molecules (with a reference to the Koopmans' theory [17]).

Since optical absorption characteristics give us ability to determine optical band gap of amorphous thin layers [18] and also are important for photoelectric measurements (such as CELIV [19] and ToF [20] methods), spectroscopic analysis of optical absorption of thermally evaporated organic layers was performed. $E_{g, opt}$ values were acquired from analysis of amorphous thermally evaporated organic thin layer absorbance spectrum according to the Tauc's law [18], which says that $E_{g, opt}$ can be derived from photon energy $h\nu$ versus $(\alpha h\nu)^{0.5}$ graph (α being an optical absorption coefficient). Some examples of optical band gap representation in so called Tauc's plot are given in Fig. 1 for materials (3c, 3d, 4a, 4f and 5b).

The values of energy level of the LUMO were calculated from the difference of values of the HOMO energy level and $E_{g, opt}$ [21]. The HOMO and the LUMO energy level values are presented in energy diagrams of Fig. 2 (in respect of 0 eV energy vacuum level). Fig. 2a energy diagram represents the HOMO and the LUMO energy level comparison among molecules in group (2) (as classified in Table 1 and Supplementary information on organic synthesis)

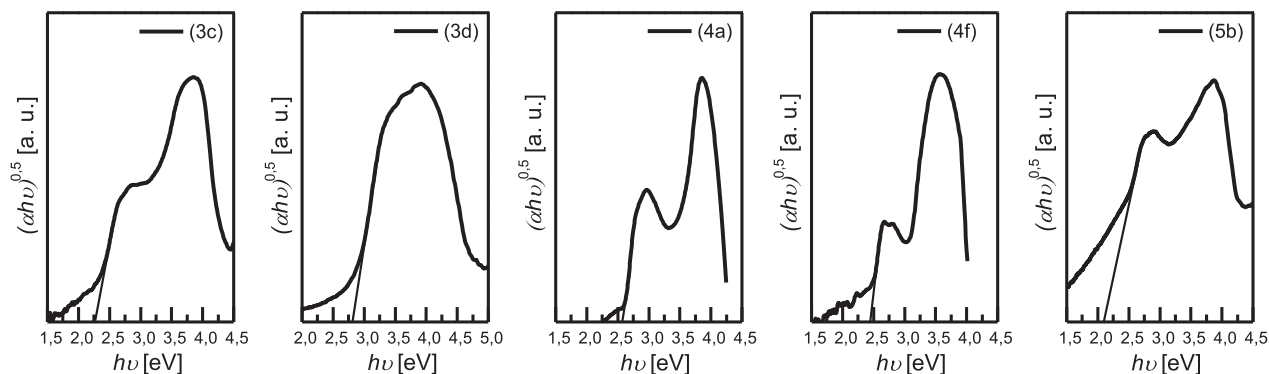


Fig. 1. The Tauc's plot of materials (3c, 3d, 4a, 4f and 5b).

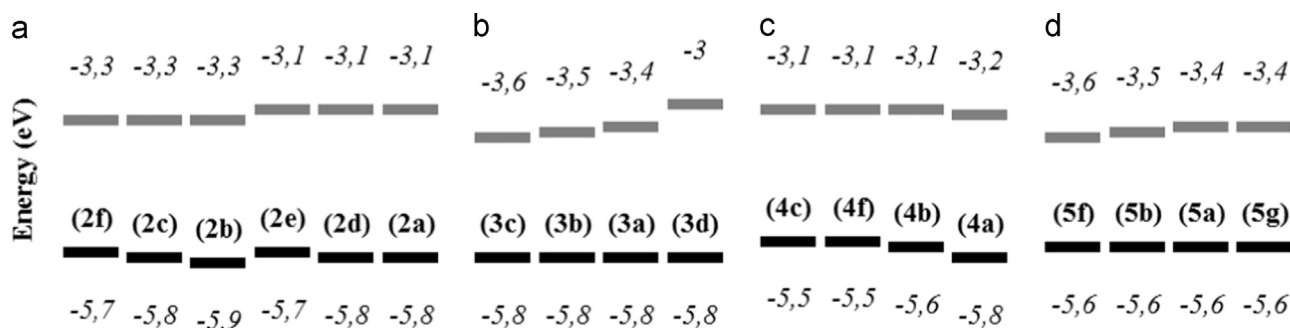


Fig. 2. The energy diagram (values of the HOMO and the LUMO energy levels with respect to 0 eV vacuum level) of materials with chlorine-a, amine-b, iminophosphorane-c and tetrazole-d substituent group.

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