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Synthesis of quinoline based heterocyclic compounds for blue lighting application

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ABSTRACT

2,4-Diphenylquinoline (DPQ), derivatives 6-chloro-2,4-diphenylquinoline (DPQ-Cl) and 4′,6-dichloro-2,4-diphenylquinoline (DPQ-Cl_2) were synthesized using a three-component domino reaction. The DPQ, DPQ-Cl and DPQ-Cl_2 were characterized by nuclear magnetic resonance spectroscopy, scanning electron microscopy, thermogravimetric analysis (TGA). Fourier transformed infra-red spectroscopy, X-ray photoelectron spectroscopy (XPS), Ultraviolet–visible (UV–vis) spectroscopy and photoluminescence spectroscopy. The TGA results showed that the DPQ was more thermally stable with respect to the DPQ-Cl and DPQ-Cl_2. The synthesized organic phosphors showed bright emission in the blue region under an UV excitation wavelength of 325 nm with the power of 18 mW. These organic phosphors were found to be efficient candidate and may be used in organic blue light emitting devices.

1. Introduction

The development of light emitting devices based on purely organic materials is a growing research field in last some decade [1,2]. The Organic phosphors (OPs) have been found to have potential applications in organic electronics [3,4], chemical and biological detection [5–7] as well as organic light emitting diodes (OLED). The organic materials based phosphors have several advantages with respect to inorganic materials such as the ease of synthesis, handling and very high quantum efficiency [7]. To develop environmental friendly, safer and more energy efficient organic phosphors for use in the lighting applications [8,9] is a challenged for the researchers. Various authors have reported the synthesis of yellow-green phosphors based on different organic materials. Organic phosphors based on 1,9-anthrapyridone, cationic dyes, 4-amino naphthalic acid and other compounds have been utilized for day-light fluorescent pigments [10–12]. Tian et al. have reported the electroluminescent properties of self-assembled polymer thin films [13]. The efficiency of organic phosphors is still relatively low when compared to their inorganic counterparts, which may be due to the highly bonded nature of the electrons in the metal-free organic materials. As a result, these materials leave little freedom for emission from triplet states. These drawbacks caused OPs to have been studied less intensively and as a result phosphorescence is considered only due to inorganic or organometallic property. Hoshino [14], Kohler [15], Reineke [16] et al. reported that the emission of metal-free-organic materials is observed to be very weak and ineffective thereby limiting their evaluation for modern phosphorescent applications [14–16]. However, the main emphasis has been given to the phosphors based on organometallic chelates [17,18]. It has been widely accepted that purely organic materials are non-phosphorescent in character. In fact, the phosphorescence in organic materials is probably attributed to aromatic carbonyls, the heavy atom effect or halogen bonding [19]. Quinolines and related heterocyclic systems represent an important class of alkaloids and are also found as structural frameworks in a large number of biologically active natural products and pharmaceuticals [20]. These nitrogen-containing heterocycles possess broad applications in drug development such as treatment of MCH (melanin concentrating hormone) receptor related disorder [21], cell proliferative disease [22], transmissible spongiform encephalopathies [23], malignant tumor, stomach cancer, brain tumor, and large intestine cancer [24] and bacterial infections in mammals [25]. Quinolines also have some usefulness in materials science [26], bio-organometallic processes [27], agrochemicals such as dyestuffs and corrosion inhibitors [20]. Additionally substituted quinolines show biological activity as antagonists of endothelin [28], $5HT_3$ [29] and NK-3 receptors [30] and also

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function as inhibitors of gastric (H^+/K^+)-AT pase [31] and dihydroorotate dehydrogenase [32].

Since quinoline derivatives are heterocyclic, various methods are available for the synthesis of these analogues especially by aza-Diels–Alder reactions [33]. Synthetic protocols reported so far, however, show some disadvantages, such as callous reaction conditions, through either multi-step reactions or expensive reagents, long reaction times, high catalyst loadings and low yields. Therefore, there is a demand for a protocol with reagent economy, one-pot process, cheap catalyst and improved yields. As an extension of our work on the synthesis of quinoline-annulated heterocyclic compounds [34], we developed a new one-pot process for the synthesis of quinoline derivatives.

The object of the present investigation was to develop an efficient blue light emitting organic phosphor using 2,4-diphenylquinoline (DPQ) modified with chlorides. The structural, morphological, thermal and luminescent properties of the metal free DPQ organic phosphors were investigated. The role of the chloro activator on the luminescent properties of the DPQ was also investigated.

2. Experimental detail

The nuclear magnetic resonance (NMR) data was recorded in a 300 MHz NMR spectrometer (Bruker). A Shimadzu SSX-550 Superscan scanning electron microscope (SEM) was used to capture the SEM images at different magnification. Thermo gravimetric analysis (TGA) curves were obtained using a TGA/SDTA851e (METTLER TOLEDO) in an argon atmosphere at a heating rate of 10 °C/min. Fourier transformed Infra Red (FTIR) spectra were recorded on a Nicolet 6700 FTIR with a 8 cm^{-1} spectral resolution. The X-ray photoelectron spectroscopy (XPS) analysis was carried out with a PHI 5000 Versaprobe-Scanning XPS Microprobe. The reflectance spectra were collected using a Perkin Elmer Lambda 950 UV–Vis photospectrometer. The photoluminescence (PL) data were recorded using a He–Cd laser at an excitation wavelength of 325 nm with a 18 mW laser power after using a band pass filter.

2.1. General procedure for the preparation of 2,4-diphenylquinolines (*4a–c*)

A mixture of amine (**1a** or **b**) (1.1 equiv.) and aromatic aldehyde (**2a** or **b**) (1.1 equiv.) was stirred in toluene at room temperature for 10 min. $BF_3{\cdot}Et_2O$ (10 mol% relative to the phenyl acetylene) phenylacetylene (**3**) (1 equiv) was added and the reaction mixture refluxed for 4 h. After completion of the reaction (TLC) the reaction mixture was cooled and a saturated $NaHCO_3$ solution (50 mL) added. The product was extracted into ethyl acetate (3 × 25 mL) and the combined organic extracts washed with brine (30 mL) and dried over (Na_2SO_4). The Na_2SO_4 was removed by filtration and the solvent by distillation under vacuum. The resulting crude product was purified by column chromatography over silica gel (60–120 mesh) using a hexane–ethyl acetate (9:1) as eluent to give the pure products (**4a–c**).

2.2. 2,4-Diphenylquinoline (*4a*)[35]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (br. d, J = 8.4 Hz, 1H), 8.24–8.22 (m, 2H), 7.94 (dd, J = 8.4, 0.8 Hz, 1H), 7.85 (s, 1H), 7.76 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.61–7.51 (m, 7H), 7.51–7.47 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.98, 149.24, 148.91, 139.75, 138.48, 130.23, 129.66, 129.62, 129.44, 128.94, 128.69, 128.50, 127.68, 126.43, 125.85, 125.73, 119.46.

2.3. 6-Chloro-2,4-diphenylquinoline (*4b*)[35]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22–8.17 (m, 1H), 7.90 (d, J = 2.3 Hz, 1H), 7.85 (s, 1H), 7.67 (dd, J = 9.0, 2.3 Hz, 1H), 7.60–7.53 (m, 2H), 7.51–7.47 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.08, 148.45, 147.27, 139.22, 137.79, 132.25, 131.79, 130.49, 129.66, 129.52, 128.96, 128.88, 128.77, 127.59, 126.52, 124.53, 120.06.

2.4. 4′,6-Dichloro-2,4-diphenylquinoline (*4c*)[35]

^{1}H-NMR ($CDCl_3$, 600 MHz) δ 8.15 (d, J = 8.9 Hz, 1H), 8.14 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 2.2 Hz, 1H), 7.79 (s, 1H), 7.67 (dd, J = 9.0, 2.3 Hz, 1H), 7.60–7.51 (m, 5H), 7.49 (d, J = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.83, 148.81, 147.29, 137.70, 137.68, 135.97, 132.57, 131.80, 130.77, 129.54, 129.21, 128.99, 128.94, 128.90, 126.65, 124.65, 119.72.

2.5. Preparation of 2,4-diphenylquinolines (*4a–c*)

As part of our on-going research on improved synthetic methodologies, a rapid and efficient synthesis of substituted quinoline derivatives *via* three component domino reaction of aldehyde, heterocyclic amine and terminal alkynes catalyzed by Lewis acid (Scheme 1) is described. This three component four step domino sequence, which was executed under conventional heating conditions, includes imine formation, nucleophilic attack by the phenylacetylene on the imine, intramolecular cyclization and aromatization was used to synthesize the various substituted quinoline derivatives.

Variation of the catalyst and solvent showed that running the reaction in refluxing toluene (110 °C) using 10 mol% $BF_3{\cdot}Et_2O$ gave the best results, while excess of amine (**1**) (1.1 eq.) and aromatic aldehyde (2) (1.1 eq.) with respect to phenyl acetylene (**3**) were also required for optimum product formation (isolated yields are given in Table 1).

The formation of the quinoline derivative is explicable in terms of the mechanism shown in Scheme 2. After formation of the imine through reaction of the amine with the aldehyde, a BF_3 imine complex **A** is probably formed through reaction of the hard Lewis acid, BF_3, with the hard Lewis base site (N) of the nitrogen containing compound allowing for attacked by phenyl acetylene to give propargylamine **B**. Subsequent complexation of the BF_3 entity to the triple bond is followed by nucleophilic attack from the *ortho*-position of the amino-containing aromatic ring leading to 6-*endo*-*dig* mode of cyclization (intermediate **C**). Intermediate **C** would then undergo 1,3-proton shift to give the dihydroquinoline intermediate (**D**), which on oxidative aromatization afford the desired quinoline derivative.

3. Results and discussion

3.1. Surface morphology

The SEM images of the DPQ and chloro-activated DPQ are shown in Fig. 1. The pure DPQ showed agglomerated particle type morphology with different shapes and noticeable pores. After incorporation of chloro groups in the DPQ, the surface morphology changed. The DPQ-Cl showed the formation of agglomerated nano rods (NRs). On the other hand, DPQ-Cl_2 showed clear NRs with varied shapes and sizes. Thus, SEM analysis reveals the variation in the surface morphologies of the DPQ and its chloro derivatives. Finally, it can be concluded that the surface morphologies of the DPQ can be tuned by varying the number of chloro groups attached with