



Synthesis of heterocyclic naphthoquinone derivatives as potent organic fluorescent switching molecules

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Abstract

Quinone is well known molecules for not only in the biological applications but which includes electrochemical and fluorescent applications too. In this paper we attempted to synthesize a series of 2-(4-amino-benzosulfonyl)-5H-benzo[b]carbazole-6,11-dione derivatives and these set of compounds were studied for their fluorescent switching properties. The title compounds were synthesized via Michael-like addition and followed by intramolecular C–C coupling. These compounds were studied for their fluorescent switching properties by using UV–vis, photoluminescence and cyclic voltogram techniques. Among all the molecules studied for their fluorescent switching properties the compounds **4a** and **6a** exhibited good fluorescent switching properties due to the presence of poor and strong electron withdrawing functional groups in the fourth position at the fluorophoric unit. All the synthesized compounds exhibited good fluorescent switching properties which were studied and confirmed by UV–vis, photoluminescence (PL) and cyclic voltogram (CV) techniques.

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Keywords: C–C bond; Palladium catalyst; 1,4-Naphthoquinone; Cyclic voltogram (CV); Molecular switches

1. Introduction

In recent years, organic photo luminescent materials draws the attention to researchers due to their wide range of potential applications of optical information

storage, photo regulated molecular switches [1–3], cosmetics [4], textiles [5], organic light emitting devices (OLED) [6,7], etc. At the same time, a photo switchable organic fluorescent material has promising application of optoelectronic, fluorescent probe and fluorescent sensor devices working on the basis of fluorescence properties and inter-conversion of chemical species under the influence of light irradiation [8–10].

Quinones are well known the photo chromic groups that have two typical forms, i.e., a color quinone form and a colorless hydroquinone form. The two forms can be converted to each other either by chemical or electrochemical stimulation. However, photo switchable fluorescence switches based on photo chromic quinones are virtually unknown. Inter conversion of quinone to hydroquinone is a reversible process in a protic media by exchanging two protons and two electrons and this

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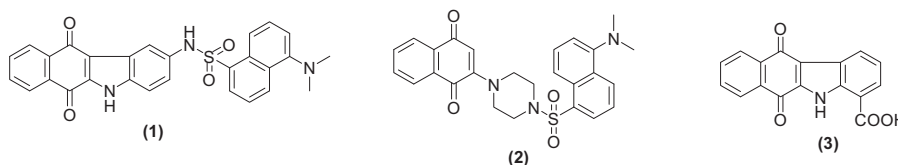


Fig. 1. Successful fluorescent switches previously reported.

redox system is the one involved in various biological electron transport systems. Quinones had proved to be good electron acceptors and hydroquinones are very good electron donors and acceptors which are already reported in literature [11–14].

Illos et al. [11,12] have been reported that the same kind of heterocyclic quinone moiety with typical synthetic procedures and dansyl chloride added as a fluorophore in the fluorophoric unit. In our previous report the simple quinone derivatives without any additional fluorophores were successfully synthesized and demonstrated for their ‘off-on-off’ fluorescent switching properties [13] (see Fig. 1). In our present work deals with novel fluorescent switches (**1a–7a**) were synthesized with simple fluorophores from 1,4-naphthoquinone which is covalently bridged to 4-amino phenyl sulfone via a simple NH spacer. The aim of the present study is to investigate, how these structural features will influence its switching photochemical properties. All the synthesized compounds were thoroughly characterized by FT-IR, ^1H NMR, ^{13}C NMR and mass spectral analysis. The fluorescent switching properties were studied and confirmed by UV–vis, photoluminescence and cyclic voltogram (CV) techniques. In our previous report the synthetic methods and physical data of all synthesized compounds (**1–7** and **1a–7a**) were reported. The same molecules were studied for their molecular binding and cytotoxicity and reported [15].

2. Experimental

2.1. Materials and methods

Melting points ($^{\circ}\text{C}$, uncorrected) of all the synthesized compounds were checked in capillary tubes by using a digital melting point apparatus (Labtronics 110, India) and found uncorrected. All the analytical grade chemicals and solvents were purchased from Sigma–Aldrich and Merck, India. Progress and completion of all the reactions were monitored by thin layer chromatography (TLC silica gel 0.25 mm, 60 G F254 and eluting solvents were ethyl acetate: hexane 1:9). All the compounds were characterized by UV–vis

spectrophotometer (UV-1800, Shimadzu, Japan) using methanol as solvent, FT-IR spectrometer (IR Prestige-21, Shimadzu, Japan) using KBr pellets, ^1H NMR spectroscopy in DMSO-d_6 (500 MHz, Bruker), and ^{13}C NMR spectroscopy in DMSO-d_6 (125 MHz, Bruker) using tetramethylsilane (TMS) as internal standard. The emission spectra of compounds **1a–7a** were studied using methanol as solvent in a fluorescence spectrophotometer (Horiba Jobin Yvon, Fluoro Log 3, Japan). A high resolution mass spectrum (HRMS-EI) was measured by Electron Ionization (EI) method (Jeol GC-Mate 2). Electrochemical redox properties of the compounds were studied by using an electrochemical workstation (CH Instruments, Inc., CH1660C, USA).

2.2. General procedures for synthesis of 2-[4-(4-amino-benzene sulfonyl)-phenyl amino]-[1,4] naphthoquinone (**1**)

2.2.1. Method A: [16]

A solution of 1,4-naphthoquinone (1.581 g, 10 mmol) in 95% of ethyl alcohol (40 mL) was gradually added over a period of 30 min, to a solution of 4-aminophenyl sulfone (2.048 g, 10 mmol) in glacial acetic acid (10–30 mL) and stirred for 30 min. Then the mixture was refluxed for 1 h. The reaction mixture was cooled and left overnight at room temperature. The black precipitates formed were separated by filtration. Water was added to the filtrate, the brownish material formed was filtered, washed with hot water (200 mL), dried at 80°C , and crystallized from 95% ethyl alcohol to give compound **1** (3.692 g, 91%) as orange crystals.

2.2.2. Method B: [17]

4-Aminophenyl sulfone (2.048 g, 10 mmol) was added to a solution of 1,4-naphthoquinone (1.581 g, 10 mmol) in water (100 mL) and refluxed for 4 h. The reaction mixture was cooled at room temperature and the brownish precipitate was filtered and washed with hot water (200 mL). The precipitate was dried at 80°C and crystallized from 95% ethyl alcohol to give compound **1** (1.657 g, 41%) as orange crystals; mp $> 300^{\circ}\text{C}$; UV–vis (acetone): 451.45 nm; IR (KBr): 1294 ($-\text{S}=\text{O}$),

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