Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 193 (2018) 492–498

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Stationary and time-resolved spectra analysis of pyrazoloquinoline derivatives with pyridyl moiety

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ARTICLE INFO

Article history:
Received 26 September 2017
Received in revised form 19 December 2017
Accepted 25 December 2017
Available online 27 December 2017

Keywords:
1*H*-pyrazolo[3,4-*b*]quinoline
Emission
CT fluorescence
Fluorescent dye

ABSTRACT

Two derivatives of pyrazoloquinoline with pyridyl moiety: 6-*N*,*N*-dimethyl-3-phenyl-1-(2-pyridyl)-1*H*-pyrazolo[3,4-*b*]quinoline (DMA-1PPhPQ) and 6-*N*,*N*-dimethyl-1,3-(di-2-pyridyl)-*1H*-pyrazolo[3,4-*b*]quinoline (DMA-1,3PPQ) were synthesized with commercial substrates. The theoretical characterization of both compounds was done. Geometry optimizations give not flat structure with the first absorption band at the wavelength about 390 nm for both compounds. Several electro-optical parameters were also calculated. The optical properties of DMA-1PPHPQ and DMA-1,3PPQ were investigated by ultraviolet-visible spectroscopy and stationary as well as time-resolved fluorescence. The fluorescence maximum and fluorescence quantum yield are strongly dependent on solvent polarity function. Results indicate CT fluorescence for both compounds. Because of high emission the investigated pyrazoloquinoline derivatives can be potential candidates for fabrications of electroluminescent devices.

1. Introduction

Chemistry of heterocyclic compounds is an integral part of organic chemistry and comprises molecules with ring structure where some carbon atoms are replaced with heteroatoms. The most important ones include oxygen, nitrogen and sulfur. Nitrogen heterocycles like derivatives of pyridine, quinoline, quinoxaline, pyrazole play important role as biologically active compounds including pharmaceuticals or pesticides. Moreover at the end of the 20th century it turned out that organic solids can be applicable as elements of electronic devices. Some nitrogen heterocycles exhibit strong emissive properties in a solution and in a solid state as well and find an application in the constructing of light emitting devices. The classical example is aluminum 8-hydroxyquinolinate used by Tang and VanSlyke as an electron transporting and emissive material in multilayer OLED [1]. Jenekhe et al. studied photoluminescent and electroluminescent properties of some poly(quinoline) homopolymers and copolymers in single or double layer devices [2,3]. The same group published a few papers concerning the application of oligoquinolines and phenantrolines as solution processable small molecules for fabrication of multilayer OLED [4–6]. Just recently this technique is drawing more and more attention due to the lower costs in comparison with high vacuum thermal evaporation processes of devices fabrication [7]. Beside fluorescent OLED emitters the phosphorescent ones are very important too. For example Ha et al. synthesized red light emitting iridium complexes with 2,3-diphenyl-4-methylquinolines and used them as dopants in multilayer devices [8]. Due to the high costs of iridium the less expensive phosphorescent heteroleptic Cu(I) complexes with quinoline derivatives were prepared by Wang and co-workers [9]. Derivatives of pyrazole like 1,3,5-triarylpyrazolines exhibit intense blue or green emission and they have been applied as optical brighteners for synthetic fibers and plastics or as scintillators [10–12]. In addition some research groups used them as emitting materials in OLEDs either as vacuum evaporated simple molecules or as polymers [13–17]. Strong emissive properties are also demanded in case of fluorescent probes synthesis. Just recently the analytical techniques based on fluorescence detection are more and more popular due to their high selectivity and sensitivity [18–20]. 8-Hydroxyquinoline is one of the most important chelating agent. This compounds itself doesn't exhibit fluorescence but after cation binding (*ex.* Al(III)) the strong emission can be observed. To increase selectivity towards various cations Hiratani joined two quinoline units with polyether chain preparing 2,2-diethyl-1,3-bis(8-quinolinoxy)propane. The significant fluorescence enhancement was observed in the presence of lithium cation [21]. It is also worth mentioning two coronands prepared from 5-chloro-8-hydroxyquinoline and diaza-18-crown-6 [22,23]. The first one was very selective for Ba(II) over Mg(II)/Ca(II) and for potassium over sodium. By contrast the second chelator was very sensitive towards magnesium cation whereas in case of Ba(II), Ca(II) no response was observed. Tsien and Pozzan synthesized quinoline

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https://doi.org/10.1016/j.saa.2017.12.066
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cryptand based fluorescent indicator for calcium(II) in suspensions of mammalian cells [24]. Mikata et al. synthesized some bisquinoline derivatives for cellular fluorescent microscopic zinc analysis based on photoinduced electron transfer mechanism [25]. Another zinc(II) sensor was based on the 8-aminoquinoline core. It exhibited high selectivity and sensitive fluorescence enhancement in the presence of an analyte [26]. O'Connor et al. investigated quinoline-2-thiol derivatives as fluorescent sensors for metals, pH and nitrogen oxide [27]. Within pyrazole derivatives some interesting fluorescent sensors for cations, anions and neutral molecules can be found too. One of the most early examples was described by deSilva and co-workers [28,29]. They designed "off-on" fluorescent podant type sensors for magnesium and calcium based on photoinduced electron transfer. Though there are quite a lot of fluorescence sensors for Cu(II) that ones for Cu(I) sensing are rare. In 2005 Fahrni and co-workers published a paper describing a pyrazoline sensors with tetrathiaza crown ether as the Cu(I) receptor [30–32]. Upon binding Cu(I) cation a 4,6–50 fold emission enhancement was observed. By contrast pyridyl substituted pyrazolines were exploited as Zn(II) sensors in aqueous media with detection limit 0.12 μm [33]. Zhang et al investigated fluoride ion fluorescence probe based on "on-off" sensing response due to desilylation of probe with fluoride ion [34]. There are some examples of fluorescent sensors for neutral molecules among pyrazolines. One of them consist of a coumarin-pyrazoline fluorophore and dinitrobnezenesulfonyl group (DNBS). Upon addition of thiols like cysteine, homocysteine or glutathione the DNBS group is cleaved and fluorescence enhancement is observed. Our research activity is focused on 1*H*-pyrazolo[3,4-*b*]quinolines PQ. We have chosen this group of compounds due to their photophysical properties especially strong emission in a solution and in a solid state as well. The detailed study of photophysical properties of 4-phenyl substituted PQs revealed that the quantum yield of fluorescence reach unity independent of solvent polarity [35]. Unsubstituted pyrazoloquinolines are predominantly blue or blue-green emitters. Introduction of a strong donor group either into carbocyclic ring or into phenyl groups attached to pyrazole ring results in bathochromic shift [36]. PQs substituted with dialkylamine or diarylamine were used as green emitters in multilayer OLEDs fabricated with vacuum evaporation techniques [37,38]. We tested PQs as potential fluorescent probes too. Thus 1,3-diphenyl-1*H*-pyrazolo[3,4-*b*]quinoline was employed to synthesize aza-crown based sensor. The crown fragment was attached either *via* methylene group to the parent fluorophore or separated with phenyl moiety. In the first case a strong fluorescence enhancement was observed according to PET mechanism. In the second one the probe exhibited bright ratiometric dual emission [39]. In one case we replaced aza-crown moiety with *N*,*N*-diethanoloamine one and the resulted sensor was sensitive but not selective towards many cations like sodium, calcium, barium, cadmium, lead and zinc. The selectivity was increased upon addition of water to acetonitrile solution [40]. The better results we received when the *N*,*N*-diethanolamine fragment was replaced with bis(pyridine-2-yl-methyl)amine one. This sensor showed a good selectivity for small inorganic cations [41]. In our recent paper we investigated photophysical properties of 6-*N*,*N*-dimethylamine-1-phenyl-3-(2-pyridyl)-1*H*-pyrazolo[3,4-*b*]quinoline [42]. Investigated compound exhibited a CT fluorescence. In this paper we present the results of further investigations where the pyrazole part was modified by introduction of one or two pyridine fragments into 1 or 1 and 3 position of pyrazolo[3,4-*b*]quinoline skeleton. In the next step we are going to investigate whether these three compounds possess chelating properties similarly to pyridyl substituted pyrazolines [43].

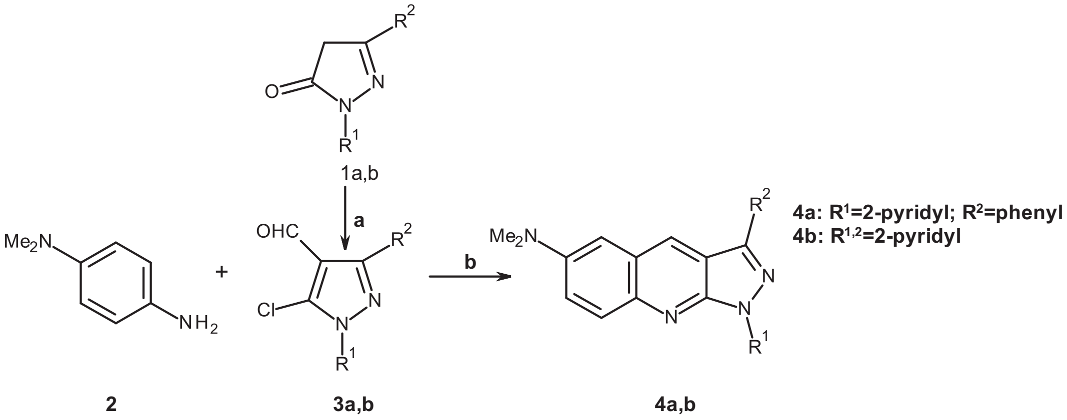
2. Experimental

2.1. Materials

The studied compounds, 6-*N*,*N*-dimethyl-3-phenyl-1-(2-pyridyl)-1*H*-pyrazolo[3,4-*b*]quinoline (DMA-1PPhPQ) and 6-*N*,*N*-dimethyl-1,3-(di-2-pyridyl)-*1H*-pyrazolo[3,4-*b*]quinoline (DMA-1,3PPQ) were synthesized in the Institute of Chemistry at the H. Kołłataj Agricultural University in Krakow. Chemical solvents for spectroscopic studies had the spectroscopic purity and were purchased from commercial vendors: *n*-hexane (HX), tetrahydrofuran (THF), dichloromethane (DCM), dimethyl sulfoxide (DMSO) – from POCH S.A.; dibutyl ether (DBE), 1-chlorobutane (CB), *n*-propanol (1-PrOH), propionitrile (PrCN), butylonitrile (BuCN), *N*,*N*-dimethylformamide (DMF), benzonitrile (BzCN) – from Fluka; chloroform (Chl), diethyl ether (DEE), methanol (MeOH), acetonitrile (ACN), 1,2-dichlorobenzene (*o*-DCBz) – from Chempur; cyklohexanone (CHxon), ethanol (EtOH) – from Sigma-Aldrich; butan-1-ol (1-BuOH) from Riedel-de-Haền and propan-2-ol (2-PrOH) from AlChem. These solvents did not show any trace of absorption and fluorescence at the used wavelength~~s~~ range.

2.2. Synthesis

Pyrazolo[3,4-*b*]quinolines **4a**,**b** were prepared by heating a mixture of aldehyde **3a** or **3b** with amine **2** within 140–180 °C according to Brack procedure [44]. Due to the harsh conditions a final pyrazoloquinoline is sometimes contaminated with side products. So to avoid the tedious purification procedures amine **2** was prepared prior to use by reduction of appropriate nitroso compound with Pd/C and hydrazine hydrate. Aldehydes **3a** and **3b** were obtained from pyrazolones **1a** and **1b** by chloroformylation with DMF/$POCl_3$ mixture. The last ones were prepared in a reaction of 2-hydrazinopyridine with ethyl benzoylacetate or ethyl 3-oxo-3-(2-pyridyl)propanoate in boiling ethanol or glacial acetic acid. (See Scheme 1.)



Scheme 1. a) $POCl_3$/DMF, 100 °C; b) 140–180 °C.