



Electronic spectra and fluorescence of dithiinodiquinoline compounds. An experimental and theoretical study



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A B S T R A C T

Absorption and emission properties of six dithiinodiquinolines 1–6 (composed of 2,3- and/or 3,4-quinolinediyl units fused with 1,4-dithiin moiety) in methanol and cyclohexane solutions were studied. Differences in fluorescence properties of the compounds 1–6 are observed, depending on the type of condensed pattern of quinoline units. Emission bands of 1 and 2 occur at wavelengths over 500 nm are shifted systematically towards shorter waves when coming from 1,2 to 3,4 and 5,6. The compounds 1–6 possess long fluorescence lifetimes of several microseconds, which can be explained by an effective electronic conjugation in the excited state. In particular, the emission spectra of 3–6 in cyclohexane show two peaks characteristic for dual luminescence. The absorption and emission properties of compounds 1–6 were discussed in terms of DFT and TDDFT calculations. The geometry optimization of the excited states results in a planar structure as compared to a folded structure in the ground state of dithiinodiquinolines 1–6.

1. Introduction

Literature data revealed that quinoline, thianthrene (dibenzo-1,4-dithiine) and its derivatives exhibit strong fluorescent properties. Some of them were even used as laser dyes [1–3]. Moreover water-soluble quinoline dyes can bind to biomolecules [4,5] and drugs [6]. The molecules marked in this manner can be used in fluorescence-optical determination methods. Polymers containing quinoline units [7,8], can be applied as pH and temperature chemosensors [9,10]. Additionally, quinoline derivatives can be also used for selective detection of Zn²⁺ ions (beyond zinc) in the brain tissues. In the same manner could be measured concentration of Zn²⁺, Hg²⁺, Cu²⁺ and other ions in natural water [11–13].

Similar properties and applications were also found for thianthrene derivatives. They were tested for light emitting polymers [14,15] or polymeric semiconductors [16,17].

Taking this into consideration we turned our attention to the previously reported dithiinodiquinolines 1–6 (Scheme 1) as both quinoline and thianthrene derivatives [18–22].

Dithiinodiquinolines 1–6 are composed of 2,3- and/or 3,4-quinolinediyl units fused with 1,4-dithiin ring (A, B and C, Scheme 1). Three different pairs of isomeric 1,4-dithiinodiquinolines are known, i.g. non-linear isomers 1 and 2, semi-linear isomers 3 and 4 and linear isomers 5

and 6. In each pair of isomers the quinoline units (B, C) are coupled with 1,4-dithiine ring in 2,3- and 5,6-positions (A) by the same (2, 5, 6) or opposite (1, 3, 4) arrangement of the azinediyl unit. Structure assignment of compounds 1–6 was proved earlier using X-ray and NMR technique [18–22].

In this work, absorption and emission properties of dithiinodiquinolines 1–6 are reported. Absorption and emission spectra were interpreted based on DFT and TDDFT calculations.

2. Experimental

2.1. Materials

1,4-dithiinodiquinolines 1–5 were isolated from quinoline sulfuration products by crystallization - compound 1 or by column chromatography (SiO₂, CHCl₃/CCl₄) - compounds 2–5, as described earlier [21]. Isomer 6 was prepared as reported in [22]. Methanol and cyclohexane were spectroscopic grade.

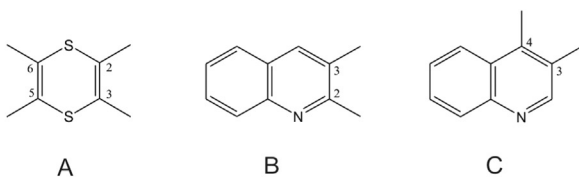
2.2. Absorption and emission spectra

Electronic absorption spectra for compounds in methanol and cyclohexane solutions were recorded on CARY – 50 UV–vis (Veria)

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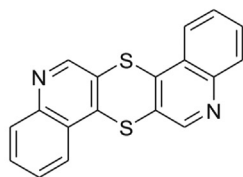
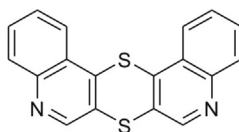
E-mail address: maria.maslankiewicz@us.edu.pl (M.J. Maślankiewicz).

structural units

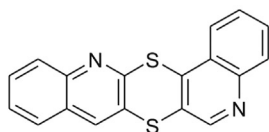


Scheme 1. Chemical structures of compounds.

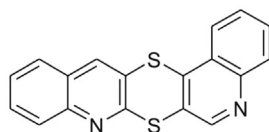
non-linear isomers

**1**1,4-dithiino[2,3-c;5,6-c']diquinoline
Thioquinanthrene**2**1,4-dithiino[2,3-c;6,5-c']diquinoline
isothioquinanthrene

semi-linear isomers

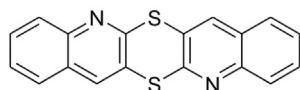
**3**

1,4-dithiino[2,3-b;5,6-c']diquinoline

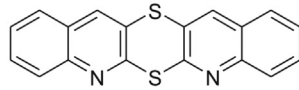
**4**

1,4-dithiino[2,3-b;6,5-c']diquinoline

linear isomers

**5**

1,4-dithiino[2,3-b;5,6-b']diquinoline

**6**

1,4-dithiino[2,3-b;6,5-b']diquinoline

spectrometer. Fluorescence measurements were performed for argon-treated solutions on a PTI QuantaMaster QM40 system coupled with tunable pulsed optical parametric oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser (Opotek Opolette 355 LD). The luminescence was dispersed by double 200 mm monochromators. The luminescence spectra were recorded using a multimode UVVIS PMT (R928) detector controlled by a computer. Luminescence decay curves were recorded and stored by a PTI ASOC-10 [USB-2500] oscilloscope with an accuracy of $\pm 1 \mu\text{s}$. All measurements were carried out for deoxygenated solutions at room temperature

3. Computational details

The calculations were performed with the use of Gaussian 09 program [23]. The DFT method with B3LYP [24] functional was used in the calculations together with 6-311+G(d,p) basis set [25,26]. The electronic spectra were computed with TD-DFT method. The solvent

environment was modeled with the PCM solvent model [27] with methanol and cyclohexane as solvents.

4. Results and discussion

4.1. Structural properties

The optimized structures of 1–6 are presented in Fig. 1. Based on crystallographic studies of 1–6 reported previously [19,20,22] it was concluded that the pentacyclic ring system of dithiinodiquinolines 1–6 is folded along the S—S vector. The experimental and optimized folding angles are collected in Table 1.

4.2. Optical properties: experimental studies

4.2.1. Absorption studies

Series of absorption spectra were recorded for solutions of

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