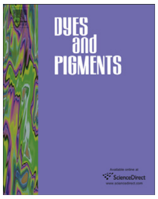
Dyes and Pigments 142 (2017) 315–322

Contents lists available at ScienceDirect

Dyes and Pigments

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



Room temperature phosphorescence lifetime and spectrum tuning of substituted thianthrenes

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ARTICLE INFO

Article history:
Received 13 January 2017
Received in revised form
22 March 2017
Accepted 23 March 2017
Available online 24 March 2017

Keywords:
RTP
RT-DFP
Phosphorescence
Thianthrene
Photophysics

ABSTRACT

A group of thianthrene derivatives has been studied to investigate the effect of different substituents and substitution positions on their photophysical behavior. Strong room temperature phosphorescence (RTP) and dual fluorescence-phosphorescence at room temperature (RT-DFP) have been observed. Compounds with efficient ($\Phi \approx 0.4$) yellow and long-lived ($\tau = 88 \pm 6$ ms) green phosphorescence have been characterized. The involvement of $n\pi^*$ and $\pi\pi^*$ states was evaluated to explain their high triplet formation yield and phosphorescent properties. To give an insight into electron properties of studied molecules cyclic voltammetry and DFT calculations have been performed.

1. Introduction

Thianthrene is a heterocyclic analog of anthracene but with two sulfur atoms substituting carbon atoms at the 9,10-positions. This structure leads to a bent, non-aromatic geometry of the central thianthrene ring [1–3]. Thianthrenes are commonly known due to their interesting electrochemical properties [3–7] and quite well studied chemistry [2,3,6,8]. Thianthrene being an electron-donor with a stable mono- and bicationic forms [4,7] has been used in several materials, including small molecules [2,6,8–11] and polymers [12,13]. Although the chemistry and electrochemistry of thianthrenes are well known, the photophysics has not been performed extensively. In particular, phosphorescent properties of thianthrene crystals have already been demonstrated [1], but no study has been performed on its derivatives. Of particular interest are the room temperature phosphorescent (RTP) properties of thianthrene, which suggests this group can be used to promote dual fluorescence-phosphorescence at room temperature in its derivatives, which brings additional interest on thianthrene based compounds. The aim of controlling and tuning luminescence of organic materials in the solid state is an attractive topic for both fundamental research, and for practical applications in several fields. For example, the observation of dual luminescence [14] e.g. dual fluorescence-phosphorescence emissions at room temperature, (RT-DFP), enhances the possibility to achieve tunable luminescent characteristics under external stimuli, which expands the potential of these compounds in photonic and optoelectronic applications.

Room temperature phosphorescence in purely organic, non-heavy-metal-containing molecules has been investigated for many years [1,15–23], and continues to be the topic of great interest, as confirmed by many recent publications, where RTP and RT-DFP are reported in several different systems [24–30]. Many of these molecules contain a non-metal *d*-electron element such as bromine, phosphorus, sulfur, tellurium or iodine, which enhances intersystem crossing from the emissive singlet state to the triplet state [15–23,31]. However, RTP or RT-DFP are observed usually in the crystalline [25] state, as powder, or in solid state blends, with the emitter dispersed in inert glassy host matrices made of amorphous polymers, such as PMMA, Zeonex® or in β-estradiol films that are non-permeable by oxygen [32]. Hosts are used to restrict the competitive thermal non-radiative decay pathways and facilitate the radiative decay of the triplet state. However, there are a few examples where surprisingly RTP has also been reported in solution [33].

While the strategies that have been implemented to restrict

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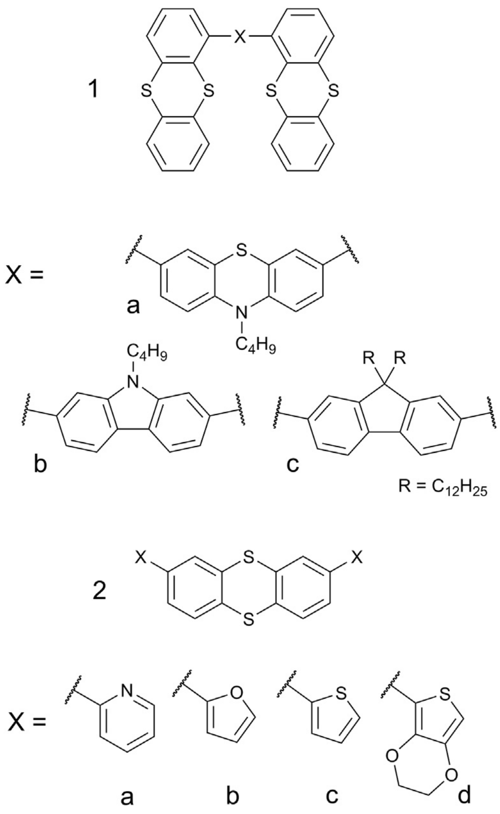
http://dx.doi.org/10.1016/j.dyepig.2017.03.049

vibrations and induce RTP have gathered some success, further work is necessary to understand the mechanism driving RTP, and achieving design rules to obtain dual emitters is even a major challenge. It is still not clear why some emitters give origin to RT-DFP and others just to fluorescence, sometimes with very similar molecular structures and in the same host [34].

The main advantage of organic materials showing RT-DFP is the possibility to achieve ratiometric measurements due to the presence of fluorescence and phosphorescence bands that are observed simultaneously. This expands the dynamic range of the emission of these compounds and introduces an internal calibration, allowing their use in applications as optical thermometry [35–37], money anti-counterfeiting techniques [38], oxygen sensors [39], analytical chemistry [40], mechanochromic materials [30], and bioimaging [41], among others.

Optimization of RT-DFP emitters involves enhancing the total luminescence yield, and achieving a large separation of the fluorescent and phosphorescent bands, which expands the colorful emission switching under external stimuli. However, increasing the separation of the two emission bands, implies achieving a large energy gap between the singlet (S_1) and triplet (T_1) excited states which negatively impacts the triplet formation yield, due to less favorable intersystem crossing, and thus giving weaker phosphorescence yield [26]. Therefore RT-DFP molecules need to be designed in a way that the intersystem crossing is enhanced, while the singlet-triplet energy is tuned to give well separated emission bands. In this study we present a group of thianthrene derivatives (Scheme 1) examining the effect of both the substitution positions and the type of substituent on their room temperature phosphorescent properties. The aim of the study is to understand structural and electronic effects, such as produced steric hindrance or donor/acceptor properties, of popular substituents on thianthrene. We further examine the effect of ππ* states on phosphorescence lifetime. Our results enabled us to understand the structure-property relationships in the RTP and RT-DFP systems based on thianthrene to further optimize the efficiency and performance of these emitters in future applications.



Scheme 1. A compendium of the thianthrene molecular structures studied in this work.

Interestingly, the phosphorescence in these thianthrenes, when dispersed in Zeonex® matrix, shows broad, featureless spectrum at room temperature. However, while compounds **1a** to **1c** are mainly RTP emitters, compounds **2a** to **2d** are dual emitters but with different fluorescence-phosphorescence ratios, with compound **2a** showing mainly phosphorescence, **2b** and **2c** showing dual fluorescence-phosphorescence bands, and **2d** showing mainly fluorescence. However, while **2b**, **2c** and **2d** have very low luminescence yields, **2a** is a strong emitter with the luminescence yield close to 40%. This is a significantly strong phosphorescence yield at RT for a metal-free pure organic emitter.

2. Materials and methods

2.1. Materials

Thianthrene derivatives were synthesized as described in previous work [3].

2.2. Photophysics

Absorption and fluorescence spectra were collected using a UV-3600 double beam spectrophotometer (Shimadzu), and a FluoroLog or FluoroMax-3 fluorescence spectrometer (Jobin Yvon). Low and room temperature measurements were acquired using a model liquid nitrogen cryostat (Janis Research) coupled with a rotary vacuum pump. Phosphorescence (PH) and prompt fluorescence (PF) spectra and decays were recorded using nanosecond gated luminescence and lifetime measurements (from 400 ps to 1 s) using a high energy pulsed Nd:YAG laser emitting at 355 (3rd harmonics) and 266 nm (4th harmonics) (EKSPLA). Emission was focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) having sub-nanosecond resolution. PF/PH time resolved measurements were performed by exponentially increasing gate and delay times. Photoluminescence quantum yield of solid films was done according to the procedure described elsewhere [42]. Blends of all materials in Zeonex® were made at 0.5–1% w/w concentration. Measurements taken at room temperature (295 ± 1 K) at all time unless stated otherwise. Fluorescence spectra in solution were recorded after degassing by 3 freeze/thaw cycles.

2.3. Electrochemistry

All measurements performed in 0.1 M Bu_4NBF_4 (99%, Sigma Aldrich) in dichloromethane (CHROMASOLV®, 99.9% Sigma Aldrich). Nitrogen bubbling was performed before measurement. Electrodes: working (Pt disc of 1 mm^2 area), counter (Pt wire), reference (Ag/AgCl calibrated against ferrocene). All cyclic voltammetry measurements conducted at room temperature with scan rate of 50 mV s^{-1}.

2.4. Calculations

DFT calculations of MO surfaces have been carried out using the B3LYP [43–45] hybrid functional combined with a 6-31G(d,p) [46–48] basis set. For all investigated compounds ground state geometries were optimized. All calculations have been carried out with Jaguar [49] version 9.1 in Maestro Materials Science 2.1 from