



Tuning the light emission of novel donor-acceptor phenoxazine dye-based materials towards the red spectral range

Mariana-Dana Damaceanu*, Catalin-Paul Constantin

"Petru Poni" Institute of Macromolecular Chemistry, Polycondensation and Thermostable Polymers Department, Aleea Grigore Ghica Voda 41A, Iasi, 700487, Romania

ARTICLE INFO

Article history:

Received 21 September 2017

Received in revised form

31 January 2018

Accepted 5 February 2018

Keywords:

Phenoxazine
Push-pull system
Red-light emitter
Pure colour
Photo-physics
Electrochemistry

ABSTRACT

A novel red fluorescent *push-pull* system able to generate an intramolecular charge-transfer (ICT) complex was synthesized. The novel dye (**R-POX**) combines some structural features which are rarely encountered in the design of other *push-pull* systems: hexyl-substituted phenoxazine as donor moiety, divinylketone as π -linker, and *p*-fluorobenzene as electron acceptor group. The relationship between the structural motif, photo-physical and electrochemical properties by UV–Vis absorption, photoluminescence and cyclic voltammetry was thoroughly investigated both as red dopant in poly(methylmethacrylate) (PMMA) or polyimide (PI) matrix, and non-doped host emitter. The molecular rigid cores of the synthesized dye formed supramolecular rod-like structures in condensed phase with a strong impact on the emissive centers. The aggregation was totally suppressed when the dye was used as dopant in an amorphous polymeric matrix, such as PMMA or PI. Electrochemical measurements revealed the dye ability for both hole and electron injection and transport. The fluorescence emission was found to be highly sensitive to solvent polarity, rendering blue-green, yellow, orange and red light emission in different organic solvents. The absolute fluorescence quantum yield reached 39.57% in solution, and dropped to 1.2% in solid state and to 14.01% when the dye was used as dopant in PMMA matrix. According to the available CIE 1931 standard, **R-POX** emitted pure and saturated red light of single wavelength with chromaticity coordinates very close to those of National Television System Committee (NTSC) standard red colour. The **R-POX** photo-optical features were compared to those of the commercial red emitter 6, 13-diphenylpentacene.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

In the past decades, organic light-emitting diodes (OLEDs) registered tremendous scientific interest and progress because of their high applicative potential in flat-panel displays to replace cathode ray tubes or liquid crystal displays, and solid-state lighting [1,2]. Due to their high efficiency, colour quality and tunability, OLEDs represent a move away from bulky bulbs and tubes, being envisaged as one of the next-generation light sources [3]. Novel light-emitting materials that give the advantages of easy synthesis and purification, low-cost solution processing, straightforward device structure and superior device performance are of interest for the development of future OLEDs [4,5]. Small organic molecule and

polymer materials are the most powerful constituents of OLEDs devices. They must fulfil some important requirements, such as high luminescence quantum yield in the solid state, good carrier mobility (both *n* and *p* type), good film-forming ability, high thermal and oxidative resistance, and good colour purity [6]. However, the efficiency and stability of OLED devices are still critical issues and lot of work is necessary to produce novel efficient OLED materials.

The most common approach in preparing white light-emitting diodes (WOLEDs) for lighting applications is to combine the three primary colour emitters, red, green and blue, or the two complementary ones, blue/yellow or sky blue/orange in a single or multiple emissive layers [7–9]. Among the three-primary colour emitters necessary to achieve reliable white light emission, much effort has been applied to find red light-emitting materials and improve their colour purity, as well as the efficiency, since their performances still lag behind blue- and green-emitters [10]. Some red-light emitters are well-known [11], being classified according

* Corresponding author.

E-mail addresses: damaceanu@icmpp.ro (M.-D. Damaceanu), constantin.catalin@icmpp.ro (C.-P. Constantin).

to the structural motif in pyran-containing compounds [12], donor-acceptor systems [13], polyacenes [14], and metal chelates [15]. However, most of the existing red emitters either display strong dipolar structure or possess extensively π -conjugated backbones, being prone to aggregation in the solid state by dipole–dipole interactions or intermolecular π – π stacking [11,16]. Thus, they become either weakly emissive or nonemissive at all in solid state. In this perspective, one of the greatest challenges remains to find red emitters with saturated colors (CIE coordinates $x > 0.62$ and $y < 0.34$, $\lambda > 630$ nm), high quantum efficiency, and robustness against thermal evaporation allowing a very fine and repeatable control of the device performances.

In order to prevent the concentration quenching, doping of an efficient red emitter into a suitable host as the emitting layer is ordinary applied to obtain high-performance red OLEDs [11,17,18]. Thus, the red emission can be generated by direct excitation of the red fluorophore or by Förster energy transfer from the excited host matrix. The tradeoff between efficient energy transfer and reduced PL quenching can be achieved through optimal dopant concentration. However, the accurate control of the doping level is very challenging and strongly limits the repeatability of devices with identical performances. Therefore, the development of red-emitters being able to emit light efficiently in a non-doped state, or even to produce emitting materials with low dependence of their properties on the doping rate when incorporated in a host matrix is a problem of tremendous interest.

One of the principal strategies utilized to date to tune the emission energy into the red ($\lambda_{em} > 630$ nm) includes the use of a *push-pull* system able to generate an intramolecular charge-transfer (ICT) complex [11], which is known to strongly absorb and emit light in the visible region [19–21]. The *push-pull* system consists of an electron donor (D) and an electron acceptor (A), which are often connected via a π -conjugated bridge that makes possible the reduction of the HOMO-LUMO energy gap. Usually, this type of fluorophore is highly polar and thus vulnerable to aggregation in solid state. However, several molecules based on triarylamine [22–24] proved to possess a pair of antiparallel dipoles, thus fluorescence quenching in solid state due to dipole-dipole interaction was substantially suppressed. Dipolar red fluorophores seem to offer much better performance than those of non-polar but extensively π -conjugated polycyclic aromatic hydrocarbons [11]. First, the existence of both electron donor and acceptor can intensify the charge-transfer absorption and emission. Second, the hole and electron carriers of the materials can be nearly balanced due to the electron acceptor in addition to the electron donor unit.

Phenoxazine (POX) is a particularly interesting heterocycle known as strong electron donor moiety. Due to its non-planar ring structure, the π -stacking aggregation and intermolecular excimer formation in the solid state is expected to be considerably reduced. Phenoxazine derivatives were barely explored as building blocks in electroluminescent materials although they are known as efficient laser dyes and display high luminescence efficiency [25–31]. Some 1,4-benzoxazino[2,3-*b*]phenoxazines were applied as hole-injection active layers in OLEDs [32]. Conjugated polymers containing phenoxazine and dialkylfluorene were used as semi-conducting layers in field-effect transistors [33]. More often, the POX unit was employed as electron donating group in dye-sensitized solar cells (DSSCs) with high conversion efficiencies [34,35]. A thorough literature survey revealed that red-light emitting materials containing phenoxazine heterocycle received little attention. Oddly, the use of electron donating POX core has been scarcely explored as a strategy to tune the emission energy to the red spectral range in *push-pull* systems [36], to the best of our

knowledge.

Herein, we report a new red phenoxazine-based dye (**R-POX**) suitable for efficient pure red light emission. Significantly, it can be easily obtained in a simple four-step synthetic route (Scheme 1) with a high overall isolated yield. This is probably one of the few red light-emitting dyes, either as a red dopant or a non-doped host emitter, having such convenient accessibility. The novel red emitter (**R-POX**) contains *N*-hexylphenoxazine as electron donor (D) unit and *p*-fluorobenzene as electron acceptor unit (A). Its morphology, photo-optical and electrochemical properties were surveyed both as red dopant in poly(methylmethacrylate) (PMMA) or polyimide (PI) matrix, and as non-doped host emitter. The obtained data were compared to those of a commercial red emitter, namely 6, 13-diphenylpentacene (**C**), acquired under identical conditions.

2. Experimental part

2.1. Starting materials

The polyimide (PI) used as host matrix for **R-POX** dye was obtained according to the procedure reported in Ref. [37]. The structure of PI is given in *Electronic Supplementary Information (ESI, Fig. S1)*. Poly(methyl methacrylate) (PMMA, $M_w \sim 350,000$) and 6, 13-diphenylpentacene were purchased from Sigma-Aldrich. Solvents were purified by standard procedures and handled in a moisture-free atmosphere. All other chemicals were of reagent grade and used as received without further purification.

2.2. Synthesis

The synthetic pathway to **R-POX** dye is outlined in Scheme 1 and the details are described as follows.

2.2.1. 10-*N*-Hexylphenoxazine (**R1**) [20,34]

In a 250 ml three-necked flask equipped with a reflux condenser, magnetic stirrer, and nitrogen inlet and outlet piping, 5 g (27.5 mmol) of phenoxazine and 80 ml of anhydrous THF were placed. The flask was immersed into an ice bath and 1.65 g (41 mmol) of NaH (60% dispersion in mineral oil) was added. The reaction mixture was maintained in the ice bath for 2 h, then 6.75 g (41 mmol) *n*-bromohexane was added dropwise for 15–20 min. The cooling bath was removed and the reaction mixture was stirred under nitrogen stream at reflux temperature for 12 h. After cooling, the reaction was quenched with 100 ml of water and the organic phase was extracted 3 times with dichloromethane (DCM). The combined organic phases were washed 3 times with water, and finally, the organic phase was dried over anhydrous Na_2SO_4 . The solvent residue was removed by vacuum evaporation and the resulting oil was purified by column chromatography using hexane:ethyl acetate = 50:1, to obtain a colorless oil. The reaction yield was 83%. ^1H NMR (DMSO, 400 MHz), δ (ppm): 6.85–6.81 (m, 2H), 6.67–6.64 (m, 6H), 3.54 (t, $J = 7.95$ Hz, 2H), 1.55 (m, 2H), 1.4 (m, 2H), 1.32 (m, 4H), 0.89 (t, $J = 7.65$ Hz, 3H).

2.2.2. 10-*N*-Hexylphenoxazine-3-carbaldehyde (**R2**) [20,34]

In a 250 ml three-necked flask equipped with reflux condenser, magnetic stirrer and nitrogen inlet and outlet piping, the Vilsmeier reagent was prepared by dropping 8.59 g (56.1 mmol) of POCl_3 over 4.1 g (56.1 mmol) anhydrous DMF kept in an ice bath. Then, 50 ml of 1,2-dichloroethane were added and the mixture was stirred for 1 h at 0 °C to get a white opalescent solution. To this solution, 3 g (11.23 mmol) **R1** dissolved in 50 ml of 1,2-dichloroethane was added dropwise under nitrogen stream for 30 min. The reaction mixture was refluxed overnight when a dark red solution was obtained, followed by cooling, quenching with water and

Download English Version:

<https://daneshyari.com/en/article/7907115>

Download Persian Version:

<https://daneshyari.com/article/7907115>

[Daneshyari.com](https://daneshyari.com)