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Published in:
 Synthetic Metals

DOI:
[10.1016/S0379-6779\(00\)01329-1](https://doi.org/10.1016/S0379-6779(00)01329-1)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
 Publisher's PDF, also known as Version of record

Publication date:
 2001

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Giro, G., Cocchi, M., Fattori, V., Gadret, G., Ruani, G., Murgia, M., Cavallini, M., Biscarini, F., Zamboni, R., Loontjens, T., Thies, J., Leigh, D. A., & Morales, A. F. (2001). Excimer-like electroluminescence from thin films of switchable supermolecular anthracene-based rotaxanes. *Synthetic Metals*, 122(1), 27-29. [https://doi.org/10.1016/S0379-6779\(00\)01329-1](https://doi.org/10.1016/S0379-6779(00)01329-1)

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Excimer-like electroluminescence from thin films of switchable supermolecular anthracene-based rotaxanes

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Abstract

Thin films of 10-[3,5-di(terbutyl)phenoxy]decyl-2-({2-[(9-anthrylcarbonyl)amino]acetyl}amino) acetate (ANTPEP), the thread of an anthracene-based rotaxane, have been processed by the spin coating technique in a polycarbonate (PC) matrix. A single layer organic light emitting diode (OLED) has been demonstrated with an external emission of 2 cd/m². The light emission, both photo- and electro-stimulated, originates from species formed in the excited state and not existing in the ground state. We assign the origin of photo- and electro-emission to molecular excimers. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electro-emission; Rotaxanes; Thin film; OLED; Excimers

1. Introduction

Organic light emitting diodes (OLED) are most promising new optoelectronic devices for practical industrial applications. Both molecular- [1] and polymeric-based OLEDs [2] have been successfully developed during the last decade. Recently, exciplex electro-emission at the interface of Alq₃-based hetero-multilayer OLEDs, which are used as voltage dependent colour tuning devices, has been claimed as a possible mechanism [3–5]. In this work we report on excimer formation and electro-emission in thin films of a novel molecular system, the 10-[3,5-di(terbutyl)phenoxy]-decyl-2-({2-[(9-anthrylcarbonyl)amino]acetyl}amino) acetate (ANTPEP). The chemical structure is shown in Fig. 1.

The investigated moiety is a basic constituent of a supermolecular system, namely the methyl-exopyridine-anthracene rotaxane (EPAR-Me), a member of a class of synthetic peptide rotaxanes [6]. Rotaxanes are a novel class of supermolecules where intrinsic functions can be designed for specific uses. Rotaxanes consist of a macrocycle constrained on a thread by two stoppers. The macrocycle could, in

principle, move from one end of the thread to the other, rotate around it or stay at one particular point on the thread. Hydrogen bonding also plays a major role both in synthesis and in determining the location of the macrocycle on the thread of the supermolecule. The ANTPEP is made of an anthracene chromophore and a bis-terbutyl benzyl system (the stoppers) covalently bonded to a peptide unit attached to a (CH₂) chain (the thread). The investigated system (ANTPEP) corresponds to the stoppers and thread of a class of peptide-based rotaxanes.

2. Experimental results and discussion

An OLED has been prepared by the spin coating technique from a suitably prepared solution of ANTPEP mixed with polycarbonate (PC) in dichloromethane. A glass substrate coated with optically transparent indium tin oxide (ITO) has been used as hole injector electrode. A high optical quality thin film, 120 nm thick, of PC/ANTPEP in different concentrations (1/10 and 1/3 in weight) has been deposited on the ITO by spin coating. This was followed by vacuum deposition of aluminium to act as an electron injector contact. Spectroscopic investigations, namely optical absorption, photoluminescence excitation profile (PLE), photoluminescence (PL) and electroluminescence (EL) have been performed in order to characterise the optical- and

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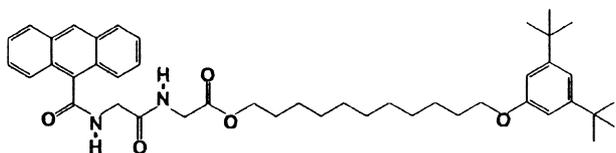


Fig. 1. Chemical structure of 10-[3,5-di(tertbutyl)phenoxy]decyl-2-((2-[(9-anthrylcarbonyl)amino]acetyl)amino) acetate (ANTPEP).

electro-emission performances and to identify the nature of the emitting species. In Fig. 1 the PLE and PL spectra measured at room temperature are reported (Fig. 2).

All the measured PLE spectra show the same features. This indicates that the emission processes have a common origin. The PLE spectra are characterised by three well-resolved peaks. This characteristic shape is reflected in the spectral behaviour of the anthracene moiety. The absorption spectrum of the PC/ANTPEP thin film gives further evidence for this behaviour as we can see in Fig. 3. The PL emission spectrum is structureless and considerably spectrally broadened (over 200 nm). A weak shoulder at around 400 nm is spectrally consistent with the PL emission of the anthracene moiety, whereas the major part of the PL spectrum is strongly red-shifted. In Fig. 3 the absorption spectrum, together with the PL spectrum and EL spectra measured at two different applied voltages, are shown. The EL shows different spectral behaviour with respect to PL.

Two different peaks appear in the EL spectra. The first is centred at the same energy as the maximum signal in the PL emission, whereas the second is at lower energy and is

broader than the former. This second peak seems to be more sensitive, both in intensity and in energy position, to the applied voltage. The maximum intensity of the spectrally integrated external EL is 2 cd/m^2 . It is worthwhile to note that the absorption, PL and PLE spectra of a 10^{-5} diluted solution of ANTPEP in dichloromethane show spectral behaviour corresponding to that of the anthracene molecule. The anthracene-like character is also still evident when working with diluted thin films, namely the 1/10 concentration in PC.

Considering the full set of experimental results, we can draw some conclusions on the origin of the emission of the ANTPEP in the thin solid film. First of all, the most “electronically active” moiety present in the ANTPEP is the anthracene unit. The absorption spectrum in fact reflects the spectral properties of the anthracene. In the PL emission spectra, features consistent with those observed in anthracene are only evident for diluted samples. The solid state, namely the thin films, is responsible for the new behaviour affecting the radiative emission of the system. The constant PLE spectrum is independent of the wavelength (from 400 to 500 nm), proving that the emission originates from a common electronic origin and not from defects, low-lying species or impurities. The anthracene absorption features are reproduced in the PLE spectra. Features related to impurities, molecular aggregates, or defects in the ground state are excluded. Analysing the PL spectra, we can assign the first broad feature to the prompt-fluorescence from the anthracene unit in the ANTPEP system. In fact, the spectral position is in agreement with the expected fluorescence from anthracene crystals. The overall broad character of the

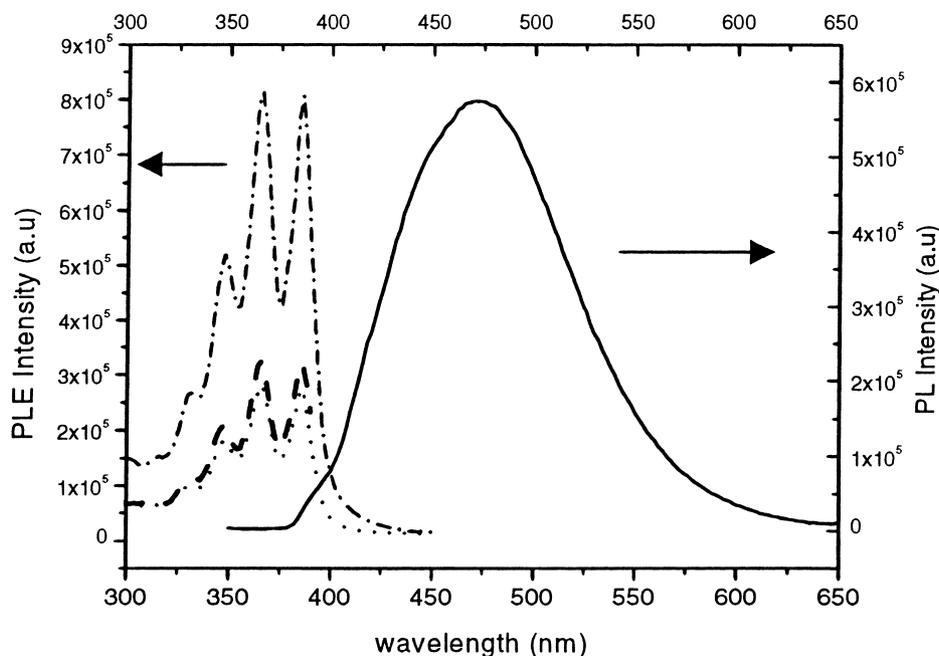


Fig. 2. PLE and PL spectra of the PC/ANTPEP 1/3 thin film. PLE spectra were obtained at 470 nm (dash-dot), 400 nm (dash-bold) and 500 nm (dot). The PL spectrum (line) has been obtained by exciting at 330 nm.

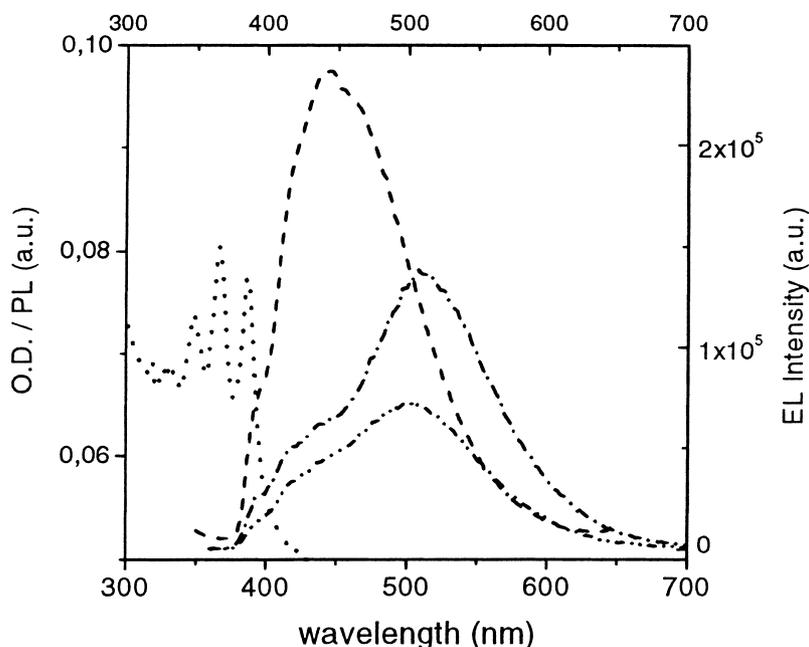


Fig. 3. Absorption spectrum (dot), photoluminescence (PL) spectrum (dashed) and electro-emission (EL) spectra at different working voltages (dash-dot, $V_0 = 28$ V and dash-dot-dot, $V_0 = 24$ V) of the PC/ANTPEP 1/3 thin film. All the spectra have been measured at room temperature.

emission spectrum is assigned to excimer emission, i.e. from species occurring in the excited states, but not in the ground state, of the solid phase of ANTPEP. At present, we do not have structural data in order to further support this assignment. Nevertheless, the spectroscopic behaviour is consistent with our conclusions [7]. Comparing PL and EL spectra, we note the correspondence between the first broad peak in the EL spectra and the PL peak (see Fig. 3). This is an indication that the nature of the emission is common for the two processes. The important conclusion to be drawn from this evidence is that both the PL and the EL of the ANTPEP-based OLED devices may be assigned to the same excimeric origin. The field dependent low-energy EL spectral feature is not completely understood, but we tentatively assign this feature to trapped charged species in the thin film. Further studies are necessary in order to more fully understand this aspect.

We should note that in our single layer OLED device there is a rather large mismatch between the ITO work function (typically 4.5–4.7 eV) and the ionisation potential of the investigated molecular system (around 7–8 eV). Nevertheless, the external light-intensity of 2 cd/m² obtained in our

OLED device is an encouraging result for further studies on this new supermolecular system.

Acknowledgements

We thank EU-TMR Project “DRUM” contract number CT97-0097 and CNR-PF MSTA II Project DEMO for financial support.

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