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Optical and electroemission properties of thin films of supermolecular anthracene-based rotaxanes

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Abstract

Rotaxanes are a new class of functional materials. They consist of mechanically interlocked supermolecular systems where a central linear thread passes through the cavity of a macrocyclic ring. The ring is constrained within the two extremities of the thread by two bulky stoppers. In this work, we report on spectroscopic characterisation of an anthracene-based novel rotaxane (EPAR-Me) and on the electroemission (EL) from a basic rotaxane component (ANTPEP). An OLED has been prepared using the anthracene-based thread (ANTPEP) of the EPAR-Me rotaxane in polycarbonate matrices. Spectroscopic measurements are reported, supporting excimer-like EL and field dependent electroexcimer for the ANTPEP thin film. Tentative assignment of emitting species of EPAR-Me are also discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: OLEDs; Organic thin film; Rotaxanes; Supermolecules

1. Introduction

The first experimental evidence for rotaxanes, and indeed the use of the term "rotaxane", appeared in an early work published by Schill and Zollenkopf in 1967 [1]. Rotaxanes are mechanically interlocked molecular systems possessing specific functions.

Schematically, they consist of a macrocycle threaded onto a "backbone" terminated at each end by two stoppers. In this way, the macrocycle is constrained on the linear molecular unit. In Fig. 1, we show the molecular structure of the methyl-exopyridine-anthracene [2] rotaxane (EPAR-Me) studied in this work. A macrocycle including two symmetric methylpyridinium groups is threaded onto a linear peptide unit covalently bonded to a (CH_2) chain which has an anthracene unit at one end and a bis-*tert*-butyl benzylic ring at the other. The macrocycle is hydrogen bonded onto the peptide unit.

This is the basic configuration resulting from the templated synthesis process [2]. The anthracene unit could act as an electron acceptor, whereas the

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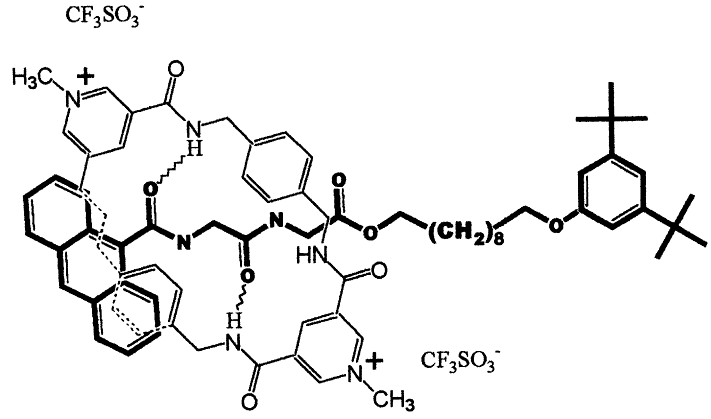

Fig. 1. Molecular structure of the investigated EPAR-Me [2] rotaxane. The units representing the thread and stoppers are indicated in bold (ANTPEP).

metylpyridinium group present in the macrocycle could act as an electron donor. Due to the unique structure of mechanically interlocked systems, there are many possible actions available to the rotaxane. For example, the macrocycle could shuttle from one stopper to the other, interact with them, or rotate around the axis of the thread. Energy transfer and electron transfer could take place in a controlled and reversible process upon external stimuli.

There have been many studies and demonstrations of these unique properties, in particular, switching and gating, but these have been conducted essentially in the liquid phase [3–5]. Our goal is to study and assess properties of this new class of unique and challenging supermolecular systems in the solid state, particularly in thin films.

In the following work, we report our results on spectroscopic characterisation and electroemission (EL) properties of the 10-(3,5-di(*tert*-butyl)phenoxy]decyl-2-{(2-[9-anthrylcarbonyl)amino]acetyl)amino}acetate (ANTPEP), i.e. the thread and the stoppers of the EPAR-Me rotaxane. Preliminary results on the photophysics of EPAR-Me rotaxane are also reported.

2. Results and discussion

Optical measurements have been performed on polycrystalline powders or on thin solid films deposited from solution by the spin coating technique. An organic light emitting diode (OLED) has been prepared to study the ANTPEP by EL measurements. A glass substrate coated with optically transparent indium tin oxide (ITO) has been used as a hole injector electrode. An 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.

The photoluminescence excitation (PLE) spectra and absorption spectra at different temperatures are reported in Fig. 2. For both ANTPEP and EPAR-Me, the absorption spectra present anthracene-like character. The spectroscopic features match the typical anthracene solid-state electronic transitions. Considering the PLE, there is a major difference between EPAR-Me and ANTPEP. While the shape of the PLE spectra follows that of the absorption spectrum for the latter species, there is a new feature peaked at 24,608 cm^{-1}, and dominating the PLE spectra of the former, which is not present in the absorption spectrum. A very weak shoulder, located at 23,077 cm^{-1}, is present in the absorption spectrum of EPAR-Me but at lower energy with respect to the low energy feature of the PLE spectrum.

The photoluminescence (PL) spectra of ANTPEP, both in solution and in thin films of ANTPEP in PC matrix at different concentrations, are shown in Fig. 3. The PL spectrum of the diluted solution shows typical

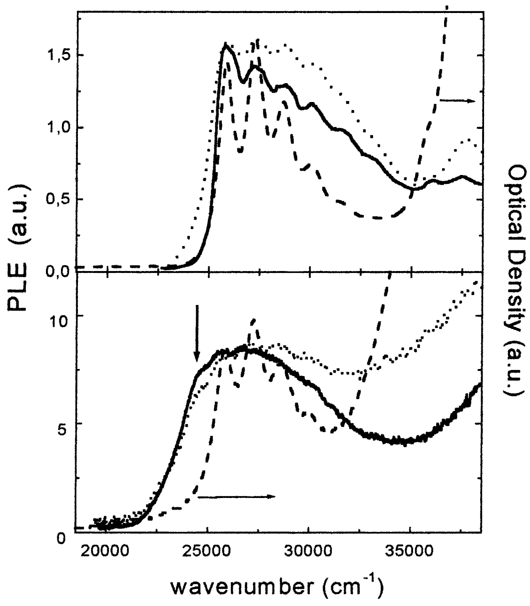

Fig. 2. PLE and Absorption spectra of ANTPEP (top) and EPAR-Me (bottom). ANTPEP: PLE spectrum at 293 K (· · ·) and at 16 K (—), absorption spectrum at room temperature (– – –). EPAR-Me: PLE spectrum at 293 K (· · ·) and at 16 K (—), absorption spectrum at room temperature (– – –) of a thin film spin coated from ethylacetate solution.

anthracene-like PL. This behaviour is also present in the spectrum of the PC/ANTPEP 1/10 film, however, increasing the PC/ANTPEP to 1/3 results in a broad, red-shifted, unstructured spectrum peaked at around 21,050 cm^{-1}. A weak shoulder is also present (at around 25,640 cm^{-1}) at the spectral position of the anthracene-like emission.

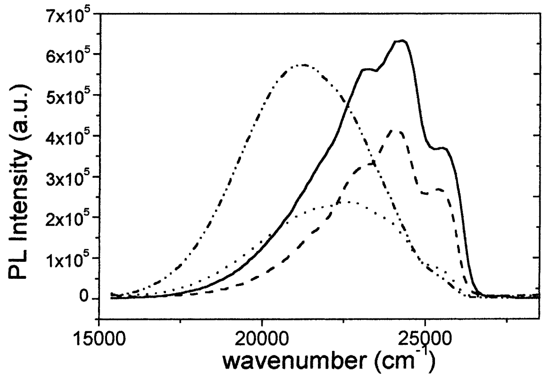

Fig. 3. Photoluminescence (PL) spectrum of ANTPEP: 10^{-5} molar dichloromethane solution (—), PC/ANTPEP 1/10 in wt.% (– – –), PC/ANTPEP 1/3 in wt.% (· · ·), and 100% spin coated thin film (– · · – · · –).

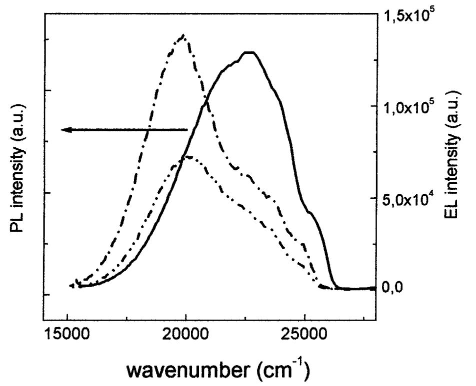

Fig. 4. Photoluminescence (PL) spectrum (—) and electroemission (EL) spectra at the different working voltages $V_0 = 28$ V (– · – · –) and $V_0 = 24$ V (– · · – · · –) of the PC/ANTPEP 1/3 thin film. All the spectra have been measured at room temperature.

The EL spectra, measured at working voltages of $V_0 = 24$ and 28 V, from the OLED device prepared with the PC/ANTPEP 1/3 thin film are presented in Fig. 4 along with the PL spectrum. Both EL spectra measured at different working voltages are similar, having two clearly visible broad peaks, however, the relative emission intensities differ. Moreover, the most intensive peak is located at lower energy (around 20,000 cm^{-1} for $V_0 = 24$ V and around 19,400 cm^{-1} for $V_0 = 28$ V) with respect to the PL structureless peak (21,050 cm^{-1}).

The PL spectrum of the EPAR-Me is reported in Fig. 5. It consists of a very broad unstructured feature peaked at around 18,000 cm^{-1} at room temperature and at 19,000 cm^{-1} at 4.2 K. Considering the full set of our experimental results, we can tentativelly 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 chromophore. 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 film, is responsible for the new behaviour affecting the radiative emission of the system. The constant PLE spectrum is independent of the wavelength (from

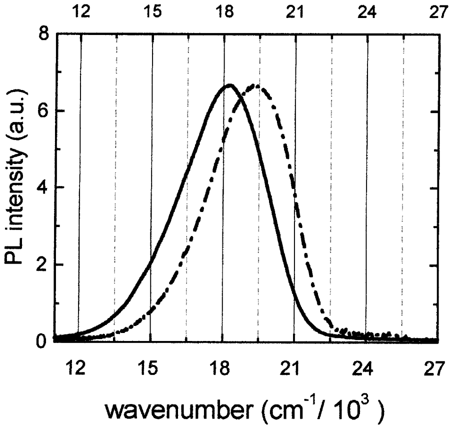

Fig. 5. Photoluminescence (PL) spectra of polycrystalline powders of EPAR-Me at 293 K (—) and 4.2 K (– · – · –). The excitation energy is 27,360 cm^{-1}.

25,000 to 20,000 cm^{-1}), 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 emission spectrum may be 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 [6]. Comparing PL and EL spectra, we note the correspondence between the positions of the first broad peak in the EL spectra and the PL peak (see Fig. 4). 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 second EL low-energy band shows relative intensity changes (with respect to the first EL band) and spectral position differences upon increasing of the applied electric field (see Fig. 4). A variation of around 20% of the applied electric field results in a doubling of the intensity of the low energy band whereas the first band intensity increase of some percent. Moreover, the location of the low energy band down-shift of 600 cm^{-1}, whereas the first band stay unchanged in energy.

The field dependent low-energy EL spectral feature is not completely understood, but seems to have a different origin from the first one, and we tentatively assign this feature to trapped charged species in the thin solid film.

Considering the EPAR-Me PLE spectrum, we should note that the presence of the new feature indicates the presence of emitting species in the ground states. The absorption spectrum shows a weak feature located at lower energy with respect to the PLE low lying state. The steady-state PL of EPAR-Me reported in Fig. 5 consist of a structureless broad band peaked at around 18,000 cm^{-1}. The characteristic vibronic progression of the anthracene moiety is totally lost and the spectrum is largely red-shifted. This behaviour suggests that even for the EPAR-Me, the emission may occur from different species involving the supermolecular nature of the investigated system in the solid state. It is worthwhile to note that the EPAR-Me in solution shows the anthracene-like behaviour. Preliminary results of time-resolved femtosecond PL spectroscopy on polycrystalline EPAR-Me show a fast energy transfer (few tenths of picoseconds) from the anthracene units to other long-living species. The unstructured largely red-shifted PL spectrum may indicate that electron transfer and/or excimer- or exciplex-like species are possibly responsible for the radiative decay process. The clear presence of low-lying emitting species in the ground state could be due to molecular aggregates (charge transfer, neutral intra- or inter-supermolecular defects, etc.) the nature of which is not yet understood. Further experiments are in progress in order to get a better comprehension of the supermolecular system in the solid state and processes occurring therein.

Acknowledgements

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References

[1] G. Schill, H. Zollenkopf, Nachr. Chem. Technol. 79 (1967) 149.
[2] A.D. Leigh, A. Murphy, J.P. Smart, A.M.Z. Slawin, Angew. Chem. Int. Edit. 36 (1997) 728.
[3] A. Credi, V. Balzani, S.J. Langford, J.F. Stoddart, J. Am. Chem. Soc. 119 (1997) 2679.
[4] V. Balzani, M. Gomez-Lopez, J.F. Stoddart, Acc. Chem. Res. 31 (1998) 405.
[5] E. Ishow, A. Credi, V. Balzani, F. Spadola, L. Mandolini, Chem. Eur. J. 5 (1999) 984.
[6] M. Pope, C.E. Swenberg, Electronic Processes in Organic Crystals, Clarendon Press, Oxford University Press, New York, 1982.