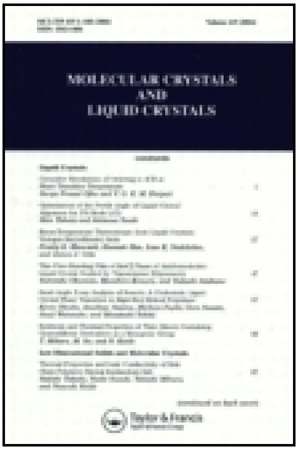

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Towards Supramolecular Assembly of Organic Solids for Optical Functions

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Towards supramolecular assembly of organic solids for optical functions

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The functions of polythiophenes as used in organic light emitting diodes and photodiodes are reviewed , with emphasis on the preparation of materials from blends and multilayers for novel optical functions such as voltage controlled colours and electroplexes.

Keywords: organic light emitting diodes; organic photodiodes; polymer optoelectronics

INTRODUCTION

The interaction of light with organic molecules in absorption and in emission processes is now increasingly being exploited in the development of novel organic materials and devices. The class of conjugated polymers is of great importance in this development, as the preparation of thin polymer films is inherently suitable for large area electronics and optoelectronics[1]. The molecular engineering of these materials, via chemical substitution, allows many degrees of freedom in preparing novel functions and enhancing old functions, for instance tuning the absorption characteristics by bandgap modulation. When combining such polymers in blends and mixtures with polymers and with organic molecules, even more extended degrees of freedom are obtained. This combinatorial universe of possible materials may include

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[1] see IEEE Trans.Electr.Devices, 44 (1997) no.8

structures built by phase separation in demixing polymer blends; it includes polymer/polymer blends with molecular miscibility, and it may include guest-host interactions in polymer/molecule blends. At the most refined level, supramolecular constructions are possible wherein a guest is assembled on a host structure, simultaneously leading to a material with desired electrical, optical and mechanical structure.

When combined with the optical processes of emission and absorption, materials for electroluminescence and for photovoltaic processes are obtained. Some of the properties in these are simple additive functions from the different contributing polymers; some are enabled by the interfaces in the structures; some require events occurring both at the interfaces and in phase separated domains. We here review a number of structures and functions. Our focus in polymers is the family of substituted polythiophenes, made soluble by the attachment of substituents on the main chain. This substitution make all of the polymers soluble, and some of them are also fusible below breakdown temperatures. Sterical hindrance due to the substituents influence the geometry of the chain; the main chain can be twisted out from planarity by substituent/substituent or by substituent/main chain interactions. This varying torsion of the main chain is equivalent to varying conjugation length and energy gap. We may thus modulate the energy position of the highest occupied molecular orbital and that of the lowest unoccupied molecular orbital, and thus the energy gap and the optical absorption features. By choice of substituents and substitution patterns we may modulate the colour of thiophenes from transparent to blue black, with absorption maxima spanning from 600 nm to 300 nm[1]. The photoluminescence from these materials also varies systematically, from 800 to 400 nm. We can therefore both generate and detect light within the visible range with these materials.

Electroluminescence from polythiophenes

These polythiophenes are very suitable for inclusion as electroluminescent polymers in polymer light emitting diodes [1-3]. Here we use a transparent indium tin oxide electrode to inject holes, a metal cathode that normally is formed by sequential deposition of Ca capped with Al. We have reported devices with electroluminescence ranging from the near infrared into the blue range. The best performing devices give external quantum efficiencies of 1 %

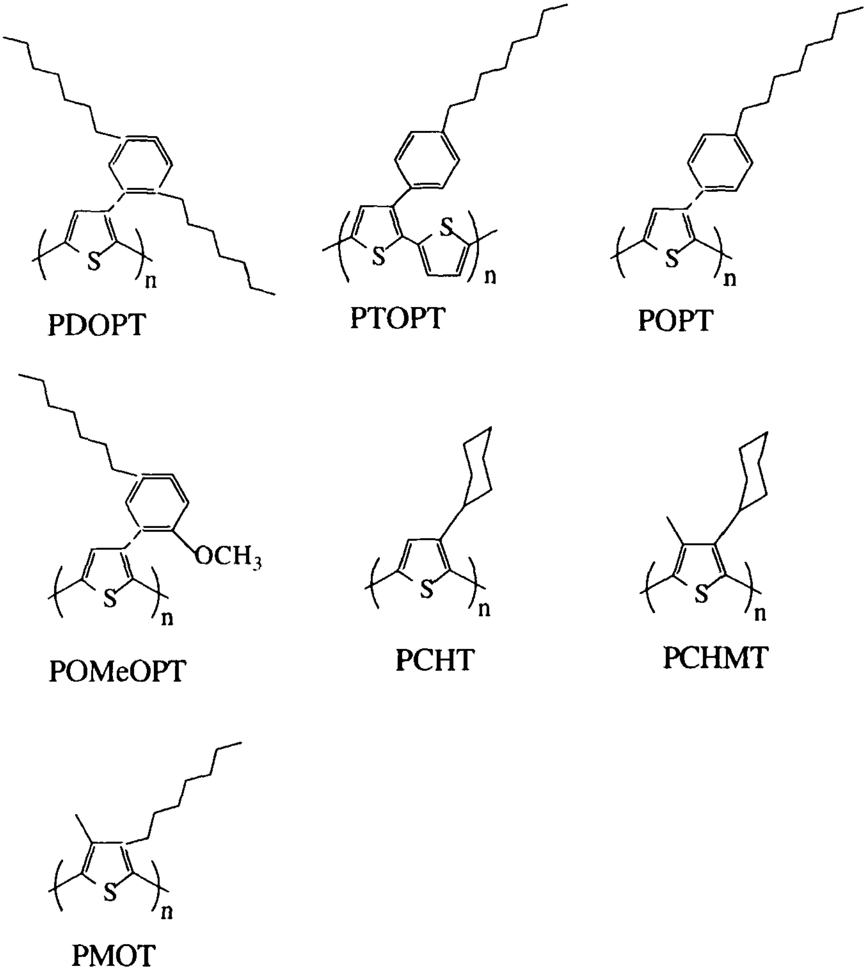

FIGURE 1 Chemical structure of polythiophenes used in these studies

photon/electrons. Some of these devices are built using double layers, to enhance injection of electrons from the cathode [4] . The layer added for this function is typically an oxadiazole, with emission in the UV range. In devices of this kind we have been able to enhance the UV emission, so as to include also UV emitting electroluminescent devices [5] . The electroluminescence emission takes place from the first excited singlet state, and is often similar to the photoluminescence(PL) spectrum. We are therefore concerned with

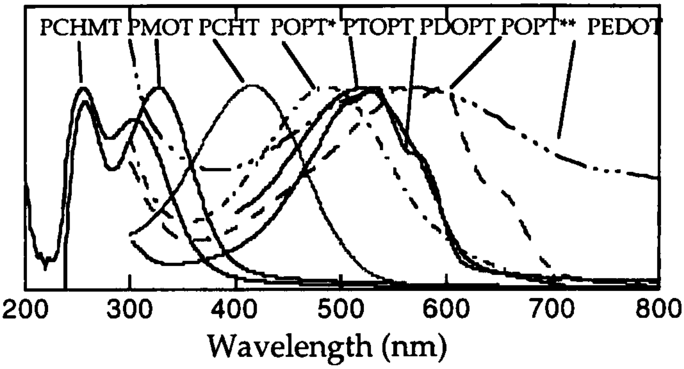

FIGURE 2 Normalized optical absorption of a number of substituted polythiophenes.

enhancing the PL yield of polythiophenes. Both in solution and solids, quantum yield vary widely with the substitution of the polymer.

Oligothiophenes in solution may give PL yields of up to 40 %, but are drastically reduced in emission intensity on condensing into a solid. The polymers we use may give PL yield in solution of 30 %, which is drastically reduced on formation of a thin film, where our highest efficiencies are 24 %. The high efficiencies are found in materials where we have designed substituents to force main chains apart, so as to reduce the possibility for radiationless recombination by fast exciton transfer between chains. This can be done with one and the same main chain, by designing the substituents properly.

The goal of chain separation may also be obtained via polymer blends. It may be accomplished by mixing a luminescent polymer into a polymer matrix[6]. By choosing a polymer matrix with strong affinity for the luminescent polymer, it is possible to obtain molecular miscibility. We have combined a water soluble polythiophene, substituted with an amino acid in the 3-position, with poly(acrylic acid), a water soluble polyelectrolyte. A molecular dispersion is obtained, and positive evidence from infrared

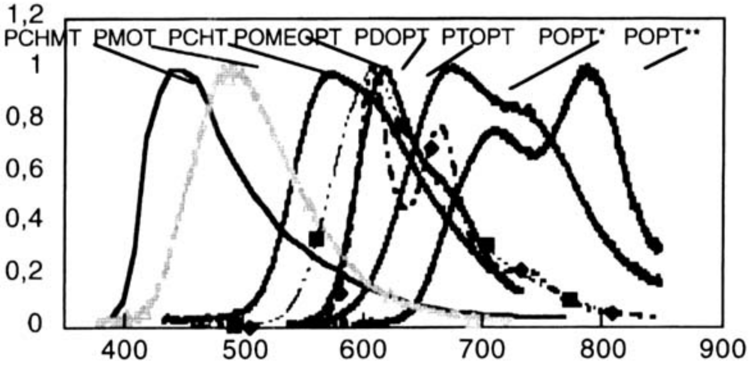

FIGURE 3. Normalized electroluminescence spectra of a series of polythiophenes, covering the full visible range. Emission in the blue may include emission from PBD, and from the electroplex at PMOT/PBD interfaces. The polymer POPT exists in two different forms, POPT** being formed by thermal annealing of POPT*.

spectroscopy and negative evidence in scanning force microscopy is consistent with this picture.

At low loading of the luminescent polymer, there is little interaction between adjacent chains, which leads to a fourfold increase of the PL yield. In addition, there is change in the PL kinetics of the process, going from a non-exponential process in the homopolymer to an almost single exponential in the polymer blends at high dispersion. The source of many of these non-radiative transitions is therefore removed in the polymer blend. Both of these materials therefore point to a common source of radiationless transitions, due to chain-chain interactions leading to dark recombination. When removing this path of recombination, PL efficiency increases.

While we here use the supramolecular assembly of conjugated main chains in a blend in order to separate the chains, there is a much more primitive approach which gives new functions, rather than enhanced performance. This is based on the important observation that polymer blends will only lead to miscible blends if the free energy of mixing ΔG is negative

$$\Delta G = \Delta H - T\Delta S$$

where the ΔH are the enthalpy and ΔS the entropy of mixing at temperature T. The last term is often quite small, as the entropy of a random coil object is small, and will very often lead to ΔG being positive. In this case we observe phase separation on some length scale. This is sometimes visible also in the optical microscope, but is very often visible only at better resolution, as in the tapping mode of scanning force microscopy. When we mix a number of soluble polythiophenes in a common solvent, and spin cast films from this solution, we thus obtain phase separation on a length scale which is larger or equivalent to the thickness of the polymer film. With such thin polymer films, it is expected that surface interactions also influence the kinetics and morphology of the polymer blend.

With a thin polymer blend film phase separating on the length range of 50-200 nm, we thus obtain a great number of individual polymer LEDs, addressed by the same voltage but with different materials of varying HOMO, LUMO and gap. In order to inject charges into these films, considerable electric fields are necessary, which also vary quite a lot with the gap - a higher gap requires a higher voltage. We therefore obtain emission from the red emitting materials only, at lower voltage than at the higher, and parallel emission from red and blue materials at higher voltage [7] . This principle applies to blends which show this columnar morphology, irrespective of the nature of the polymer, and we may therefore combine emission from (any) number of polymers in an additive manner. The efficiency of electroluminescence may vary between the different colours, and we may therefore have problems in balancing the contributing emission colours. In addition, the width of the emission spectra of the contributing polymers limits the tunability of the composite colour. Tracking the path of a polymer LED with voltage controlled colours through the colorimetric triangle shows that we may easily traverse from red to blue [8] , and hit the white point [9] but not as easily reach the green range with present day materials. This is more a reflection of poor EL efficiency in the green range than of a fundamental limitation.

Another possibility is that of blending an electroluminescent polymer with a non-luminescent and insulating polymer. If a similar phase structure is obtained, we expect to see emission from small islands of EL polymer in a dark sea of insulating polymer. This is a rapid approach to make submicrometer sized polymer LEDs, by using the phase separation properties of polymer blends. We have obtained polymer nanoLEDs with dimensions of 50 - 200 nm, which we certainly cannot resolve in our optical microscope but only in the scanning force microscope image of the emitting phases [10].

In blends we have obtained enhanced external efficiencies for electroluminescence, better than 1 %. These blends are characterised by a much more complex morphology than we use in the simple columnar structures. While there is still voltage control of colour in these blends, the enhanced efficiency is not fully explained, but may be related to the much more complex morphology. If the polymer film are thicker than the dimensions of the smaller domain, we may expect to obtain stacked layers of different polymers on top of each other. Such double layer structures have been used for enhancing the emission efficiency of polymer LEDs [11].

The control of injection and transport of charge carriers by hole-blocking and electron transporting layers is well known in the field, and is in our case necessary in order to obtain blue light from polythiophene devices. In our devices with the oxadiazole PBD as contact to the blue polythiophene PMOT, we have observed different colours, none of which is identical to the emission of the two contributing materials. Extensive simulation have located the light source at the interface between the two organic layers; interference between the light emitted from this thin interface and reflected in the metal cathode, and that immediately emitted towards the transparent anode can fully explain the spectral character of emission. Therefore interference can modulate the emission colour[12], even without using a high quality microcavity.

The reverse function of these organic materials are found in photodiodes. Here light is absorbed, and excitons generated. Photoinduced charge transfer can dissociate the exciton, and this may happen at the interface to a metal, or in molecule-molecule contact. Subsequent to charge separation, electron and hole should be transported to separate electrodes in order to generate a photocurrent. The study of photoinduced charge transfer from conjugated polymers to fullerenes[13] has shown that this process can be exploited in photodiodes. Polythiophenes have also been used in these studies, and have the advantage that the range of optical absorption is wider than with some of the other polymer families. Another advantage may be the absence of a vinyl linkage, that could be susceptible to degradation. As photodiodes are exposed to light, photochemistry must be avoided to prevent materials breakdown.

We have designed a polythiophene (POMeOPT) which interact with C_{60}, and thus can be dissolved into solid films together with C_{60}. By this approach, we obtain materials with no discernible structure, as seen with the scanning force microscope. While this material gives poor performance in ITO/polymer/Al diodes, because of large dark currents, we can add another polythiophene into the solid film, that gives better photodiode performance. The blend of these two polythiophenes gives phase separation, visible even on the optical microscope resolution. This is removed as C_{60} is added to the blend; in this context we may call C_{60} a "compatibilizer". This material gives good photodetection performance, with an quantum efficiency (electrons per incident photon) of 15%[14] .

In summary, the versatility in design of polythiophenes for bandgap engineering, structural control and phase separation/miscibility, gives us novel optical devices such as voltage controlled colours sources, but also enhanced performance in light emitting diodes and photodiodes.

Acknowledgements

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