Polyrotaxanes based on π-conjugated backbone for micro/optoelectronic applications

Project number PN-II-ID-PCE-2011-3-0035

Contract number 141 din 25/10/2011

ABSTRACT

In the past decade, it has been witnessed for remarkable innovations and progresses in polymer science, including those in the field of supramolecular science as complementary field, which offer great opportunity for new concepts, new materials with unique properties and novel practical applications. The construction of mechanically interlocked molecules such as conjugated polyrotaxane structures has attracted considerable attention over the last decades due to their architectures and topologies, but mostly because they provide an efficient strategy to achieve an “insulation” of individual molecular wires. π-Conjugated polyrotaxanes are supramolecular architectures consisting of π-conjugated backbones (guest molecules) encircled by macrocyclic host molecules through non-covalent interactions. The synthesis of such supramolecular structures is based on the molecular recognition principle and is the result of the cooperation of various non-covalent interactions. As results of reduced aggregation tendency, conjugated polyrotaxanes may function as model compounds for study of fundamental photophysical properties of various conjugated polymers. The threading of macrocyclic molecules onto the conjugated chains does not disrupt the π-conjugation and can additionally improve the solubility, as well as the morphological characteristics of the resulting complex polymers. Additionally, the synthesis of such supramolecular structures leads to distinct improvements in the thermal stability, better film forming ability combined with a high transparency and lower quenching effect when are protected from the environment by physical complexation with macrocycle molecules

PROJECT MANAGER

Dr. Aurica Farcas
"Petru Poni" Institute of Macromolecular Chemistry- Iasi
Tel: 0232-260332/141, E-mail: afarcas@icmpp.ro

TEAM MEMBERS

Dr. Ana-Maria Resmeriță
Dr. Iuliana Stoica
Drd. Mihaela Balan

OBJECTIVES - 2015

1. Preparation of a glass/TCO/ZnO/PF-BT/Ag hybrid structure

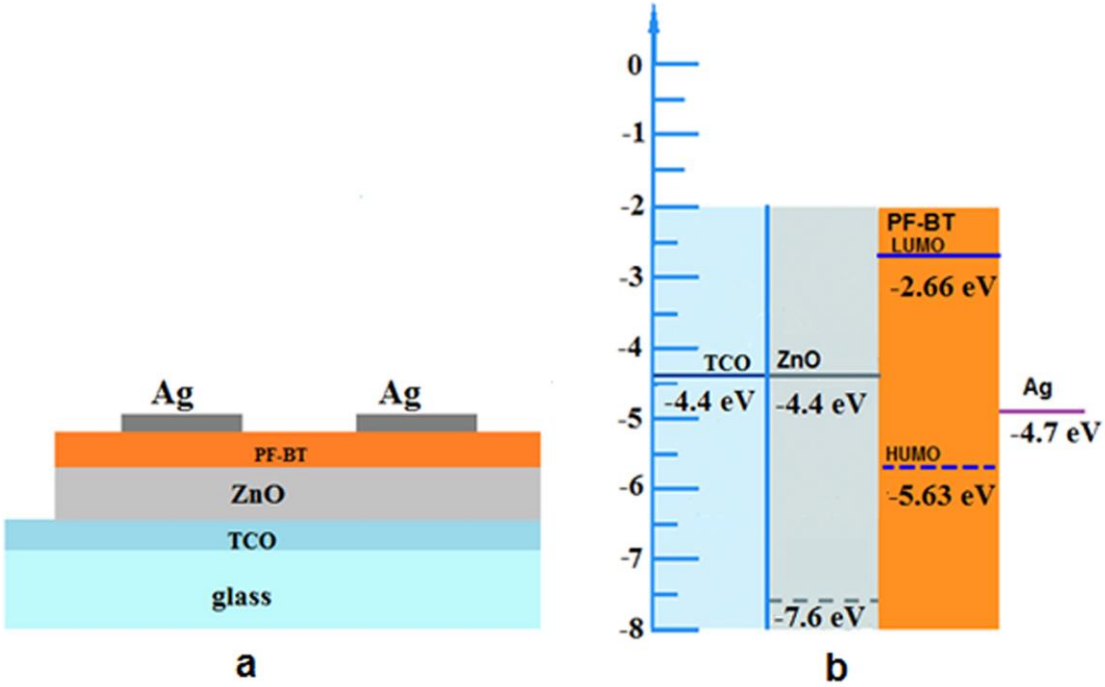
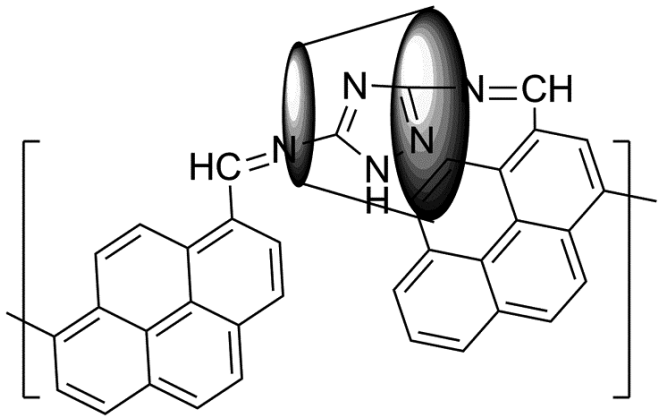


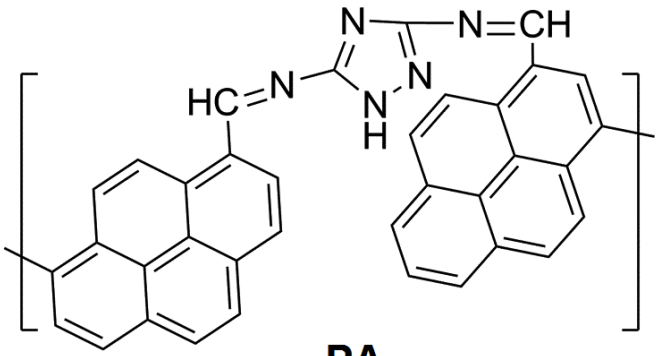
FIGURE 1. (a) The schematic illustration of the hybrid structure; (b) energy levels of the investigated hybrid structure ZnO/PF-BTcopolymer.

PF-BT layers were deposited on the TCO/ZnO substrates by spin-coating from a concentrated tetrahydrofuran (THF) solution. In such a structure, Ag was used as a top electrode and a transparent electron conducting layer (TCO) a bottom electrode. Figure 1 illustrates the schematic representation of the investigated glass/TCO/ZnO/PF-BT/Ag hybrid structure. In this configuration electrons are collected by the bottom electrode, while the holes by the top electrode.

2. Azomethine persylilated α-cyclodextrin main-chain polyrotaxanes

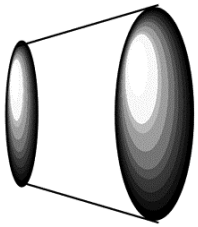


PA·TMS-αCD

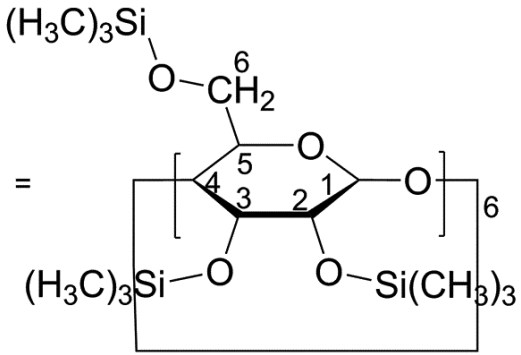


PA

where



=



TMS-αCD

FIGURE 2. Chemical structures of the polyrotaxane **PA•TMS-αCD** and its reference **PA**.

TMS-αCD encapsulation of PAMs backbones leads to distinct improvements in the solubility, molecular weights, film forming ability and thermal stability. The optical investigations confirmed that the polyrotaxane exhibited higher fluorescence quantum yield and fluorescence lifetime.

3. Polyfluorenes encapsulated into permodified cyclodextrin derivatives

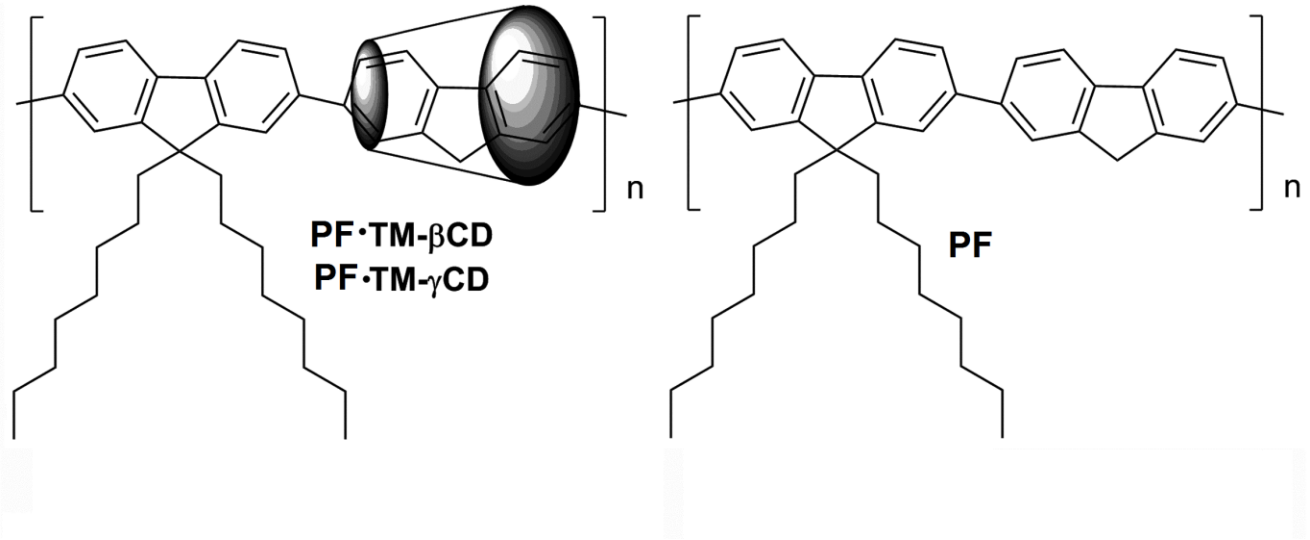


FIGURE 3. The chemical structures of the polyrotaxanes **PF·TM-βCD** and **PF·TM-γCD** and its non-rotaxane **PF** counterpart

TM-βCD or TM-γCD encapsulations of PF backbones lead to distinct improvements in the solubility, molecular weights, film forming ability associated with enhancements of the transparency of the solid films and thermal stability. The optical investigations confirmed that the encapsulated compounds exhibited higher PL and fluorescence lifetimes. These complex architectures showed interesting electrochemical characteristics, which were consistent with optical and surface morphological results. The slightly lower ΔE_g value for **PF·TM-βCD** was associated to the better charge injection between the polyrotaxane films and the electrode surfaces. In addition, HUMO/LUMO energy levels proved that all copolymers are electrochemically accessible in an electroluminescence configuration cell.

Results 2015

A. Published Papers in ISI Journals

1. A. Farcas, P.-H. Aubert, J. Mohanty, A. I. Lazar, S. Cantin, W. M. Nau
Molecular wire formation from poly[2,7(9,9-dioctylfluorene-alt (5,5'-bithiophene/cucurbit[7]uril)] polyrotaxane copolymer
European Polymer Journal, *62*, 124–129, **2015**

2. A. Farcas, A.-M. Resmerita, P.-H. Aubert, I. Ghosh, S. Cantin , W. M. Nau
Synthesis, photophysical, and morphological properties of azomethine-persylilated α-cyclodextrin main-chain polyrotaxane
Macromolecular Chemistry and Physics, *216*, 662−670, **2015**

3. L. Ghimpu, T. Potlog, A.-M. Resmerita, I. Tiginyanu, A. Farcas
Structure and morphology of nanoporous ZnO and dark current-voltage characteristics of the glass/(TCO)/ZnO/poly[2,7-(9,9 dioctylfluorene)-alt-(5,5'-bithiophene)/Ag structure
Journal of Applied Polymer Science, 132 (33), **2015**, DOI: 10.1002/APP.42415

4. A. Farcas, G. Tregnago, A.-M. Resmerita, P.-H. Aubert, and F. Cacialli
Synthesis and photophysical characteristics of polyfluorene polyrotaxanes
Beilstein Journal of Organic Chemistry, Manuscript ID 8230212, accepted for publication

B. International conferences

1. A. Farcas

Molecular wire formation from poly[2,7(9,9-dioctylfluorene-alt (5,5'-bithiophene/cucurbit[7]uril)] polyrotaxane copolymer

*Europolymer Conference (*EUPOC 2015), Conducting polymeric materials, 24-28 mai 2015, Gargano-Italia

2. A. Farcaş, A.-M. Resmerita, P.-H. Aubert

Effect of permodified cyclodextrin encapsulations on the photophysical properties of conjugated polyrotaxanes

European Conference on Cyclodextrins (Euro CD 2015), 6-9 octombrie 2015, Lille Franta

C. International poster

1. A.-M. Resmerita, A. Farcas

Synthesis, photophysical and morphological properties of azomethine persilylated α-cyclodextrin main-chain polyrotaxane

*Europolymer Conference (*EUPOC 2015), Conducting polymeric materials, 24-28 mai 2015, Gargano, Italia

D. Book

Aurica Farcas
Conjugated polyrotaxanes for optoelectronic applications
LAMBERT Academic Publishing
OmniScriptum GmbH@Co.KG
ISBN: 978-3-659-77427

E. Chapters book

1. Aurica Farcas, Pierre-Henri Aubert
Electrochemical studies of conjugated polyrotaxanes and their unthreaded analogues
Encyclopedia of Physical Organic Chemistry, chapter 24, John Willey & Sons. Inc
ISBN: 978-3-527-33668-5
2. Aurica Farcas, Ana-Maria Resmerita
Supramolecular chemistry: synthesis and photophysical characteristics of conjugated polyrotaxanes
Encyclopedia of Physical Organic Chemistry, chapter 25, John Willey & Sons. Inc
ISBN: 978-3-527-33668-5