SUPRAMOLECULAR ORGANIC SEMICONDUCTING MATERIALS FOR OPTOELECTRONICS

Acronim: SUPRAMOL-MAT

Scientific Report STAGE 2 / 2023

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Objectives

We propose here the following two main objectives followed by seven main activities:

O2. The synthesis of pseudo- and polyrotaxanes architectures based on poly(3,4-ethylenedioxythiophene) (PEDOT) and permodified or native cyclodextrines;

O3. The synthesis of the reference poly(fluorene-thiophene-phenylene-azomethine) (PFTPA) alternating copolymer .

(A1) Synthesis of PEDOT-TMeβCD, PEDOT-TMeγCD, PEDOT-βCD and PEDOT-γCD and their physical characterizations;

(A2) Exploring interactions of their soluble fractions in water with aerolysin nanopore;

(A3) Evaluation of PEDOT-TMeβCD, PEDOT-TMeγCD, PEDOT-βCD and PEDOT-γCD photophysical properties;

(A4) Electrochemical properties of PEDOT-TMeβCD, PEDOT-TMeγCD, PEDOT-βCD and PEDOT-γCD;

(A5) The photovoltaic performance of the devices based on PEDOT-TMeβCD and PEDOT-TMeγCD;

(A6) Electrical properties of PEDOT-TMeβCD, PEDOT-TMeγCD, PEDOT-βCD and PEDOT-γCD;

(A7) The synthesis of the thiophene-phenylene-azomethine (TPA) comonomer and its chemical characterization.

O2 - 2023

The synthesis of pseudo- and polyrotaxanes architectures based on poly(3,4-ethylenedioxythiophene) (PEDOT) and permodified or native cyclodextrins

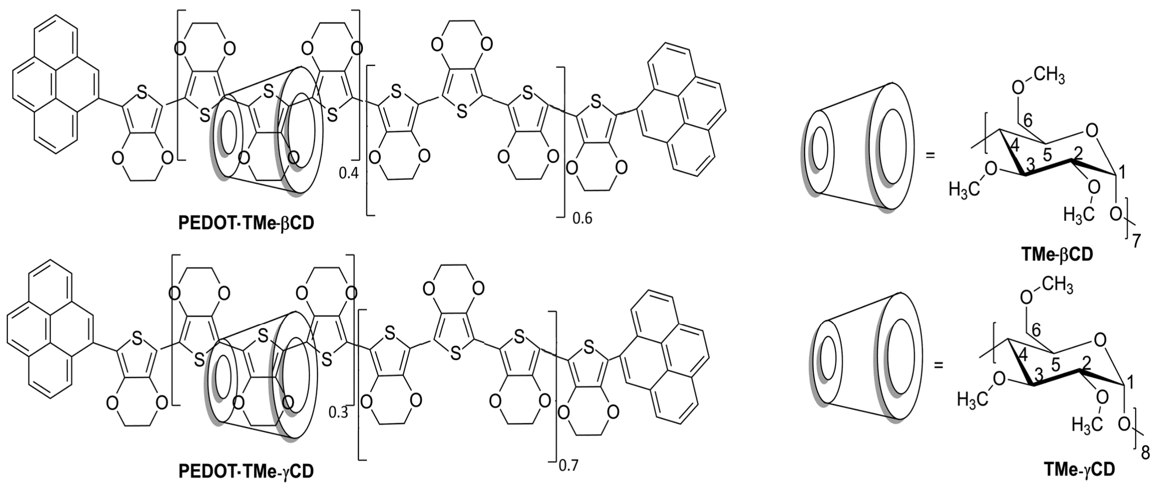


FIGURE 1. Chemical structures of PEDOT·TMe-βCD and PEDOT·TMe-γCD

O3 - 2023

The synthesis of the thiophene-phenylene-azomethine (TPA) comonomer and its chemical characterization

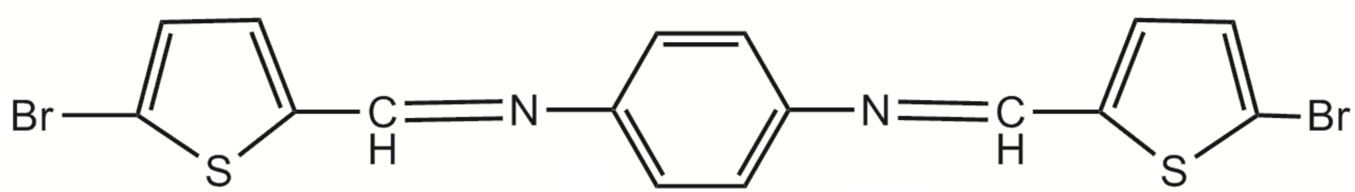


FIGURE 2. Chemical structure of TPA comonomer

(A1) Synthesis of PEDOT-TMeβCD, PEDOT-TMeγCD, PEDOT-βCD and PEDOT-γCD and their chemical characterizations

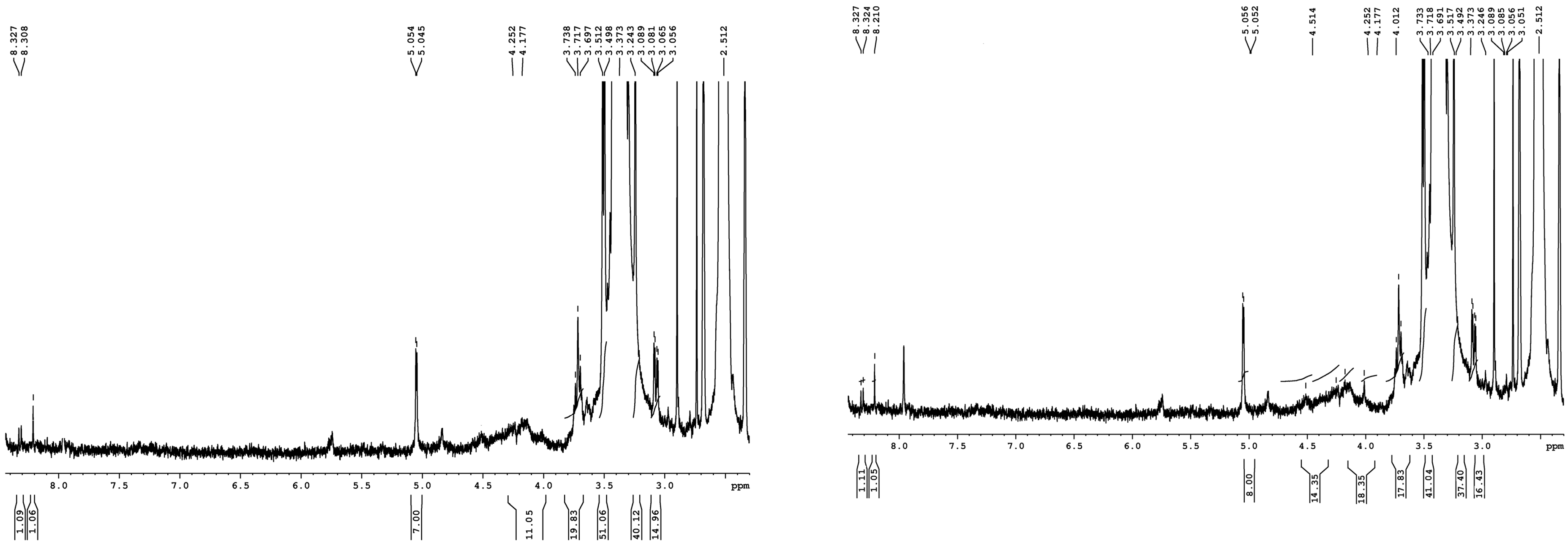


FIGURE 3. 1H-NMR spectra of PEDOT·TMe-βCD (left) and PEDOT·TMe-γCD (right).

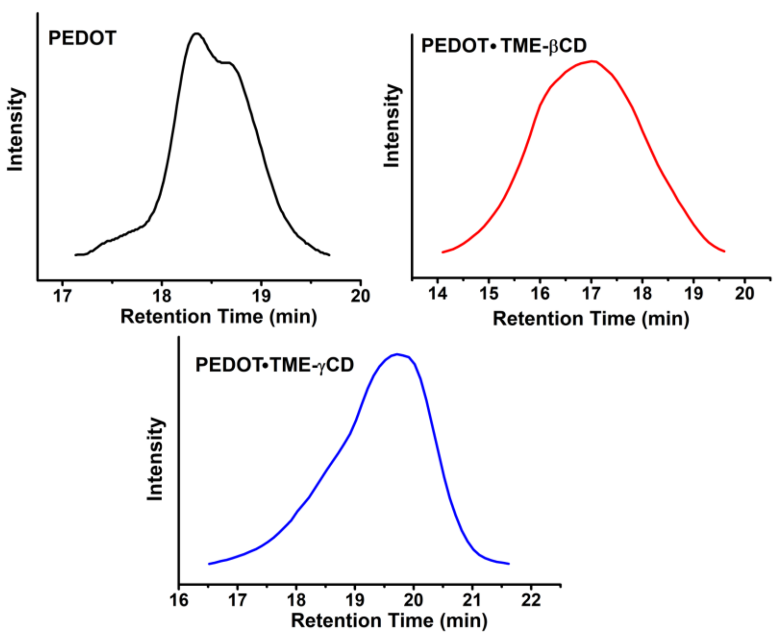


FIGURE 4. Comparison between the chromatograms of PEDOT, PEDOT·TMe-βCD and PEDOT·TMe-γCD.

(**A2**) Exploring interactions of their soluble fractions in water with aerolysin (AeL) nanopore

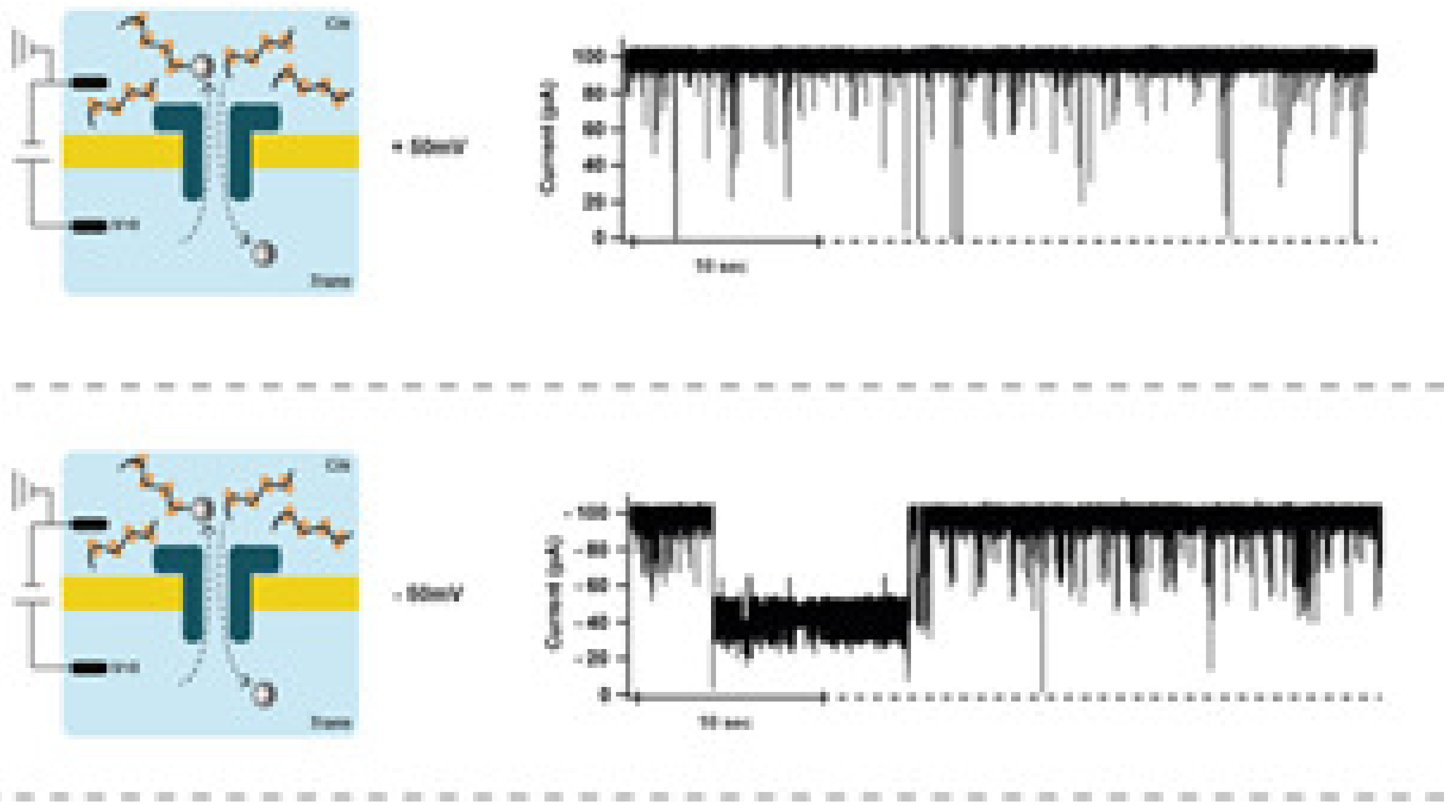


FIGURE 5. Electrical detection of PEDOT·TMe-βCD PR using the AeL nanopore. Illustration of the experimental setup used for the analysis of the PEDOT·TMe-βCD PR molecules added in the *cis* compartment in the presence of an Ael nanopore inserted in a lipid bilayer. Portions of a typical current traces recorded in the presence of 0.6 mM PEDOT·TMe-βCD PR molecules under positive + 50 mV (a) and negative -50 mV (b) trans applied voltage.

Our results demonstrate the real-time detection and high binding ability at negative voltage of PEDOT·TMe-βCD compounds to the pore lumen of Ael at a single molecule level.

(A3) Photophysical properties of PEDOT-TMeβCD, PEDOT-TMeγCD, PEDOT-βCD and PEDOT-γCD

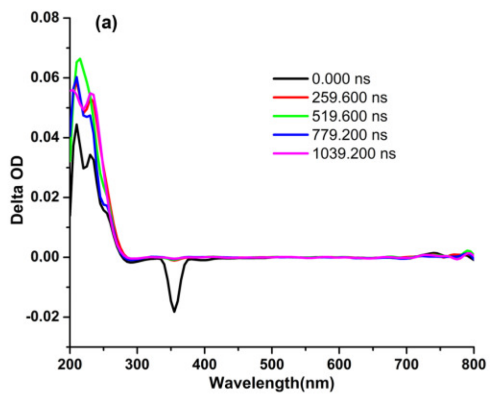


FIGURE 6. Nanosecond transient absorption of PEDOT·TMe-βCD in H2O (λex = 375 nm) (a) and ACN (λex = 355 nm) (b).

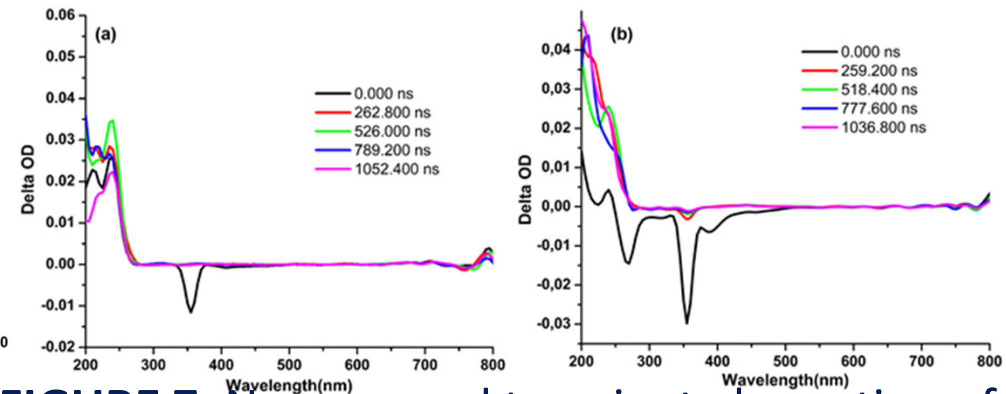


FIGURE 7. Nanosecond transient absorption of PEDOT·TMe-γCD in H2O (λex = 375 nm) (a) and ACN (λex = 355 nm) (b)

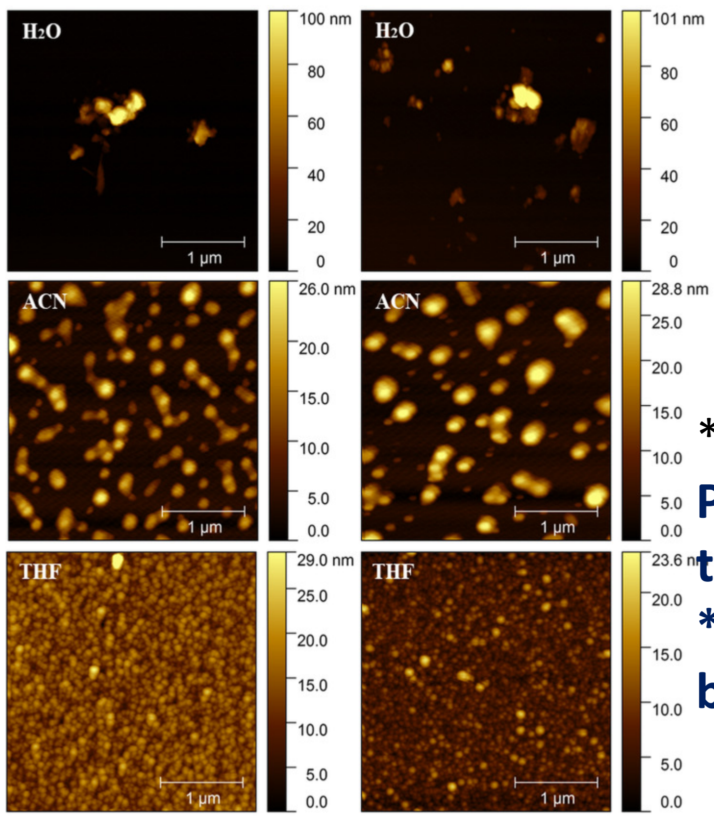


FIGURE 8. The AFM surface morphology over area of 3 × 3 µm2 of PEDOT·TMe-βCD (left) and PEDOT·TMe-γCD (right) films obtained by drop casting from H2O, ACN and THF.

***The optical results indicated that PEDOT·TMe-βCD and PEDOT·TMe-γCD are sensitive to the polarity changes of the microenvironment.**

***These encapsulated PEDOT compounds exhibited better ΦFL and ΦPH efficiencies in ACN than in H2O.**

(**A4**) Electrochemical properties of PEDOT-TMeβCD, PEDOT-TMeγCD, PEDOT-βCD and PEDOT-γCD

Cyclic voltammograms of PEDOT·TMe-βCD and PEDOT·TMe-γCD

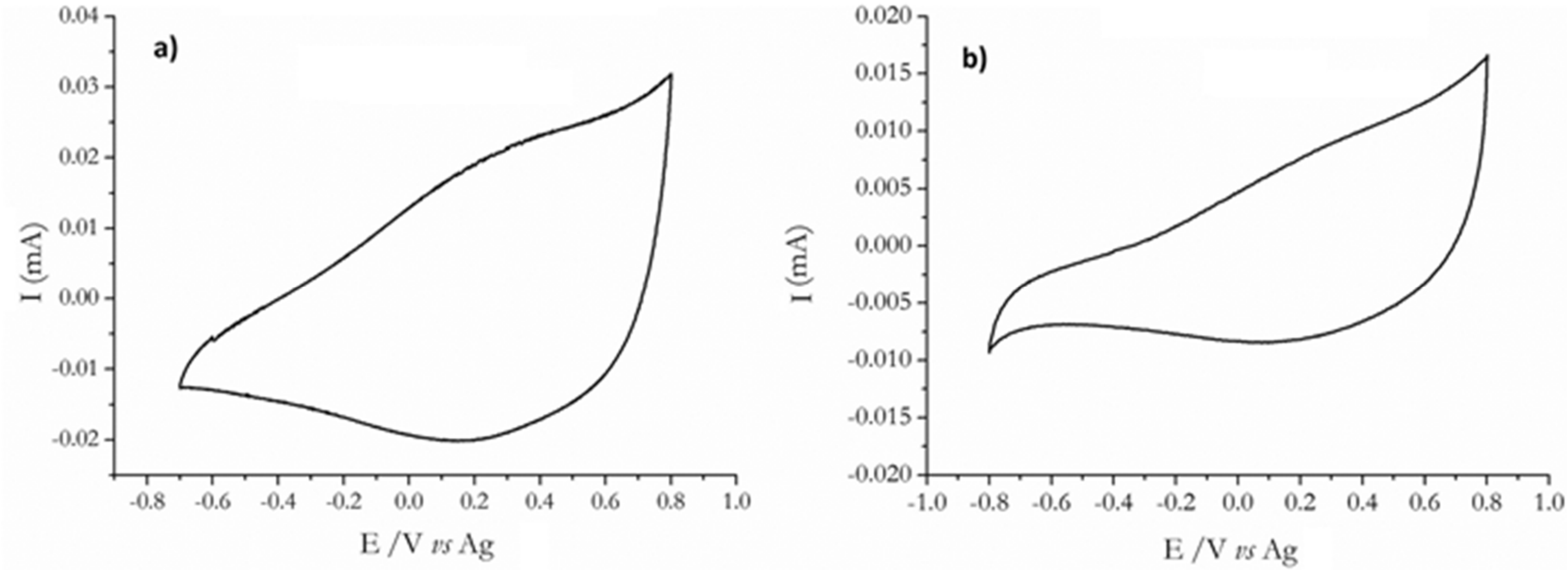


FIGURE 9. CV of PEDOT·TMe-βCD (a) and PEDOT·TMe-γCD (b) in 0.1 M TBAClO4)/ACN solution at scan rate 20 mV·s-1.

Accordingly to the electrochemical results, it can be conclude that the investigated PEDOT·TMe-βCD and PEDOT·TMe-γCD exhibit typical insulating behavior in a wide range of potential between n- and p-doping processes, denoting their semi-conducting properties.

(**A5**) Preliminarily photovoltaic results of PEDOT-TMeβCD and PEDOT-TMeγCD

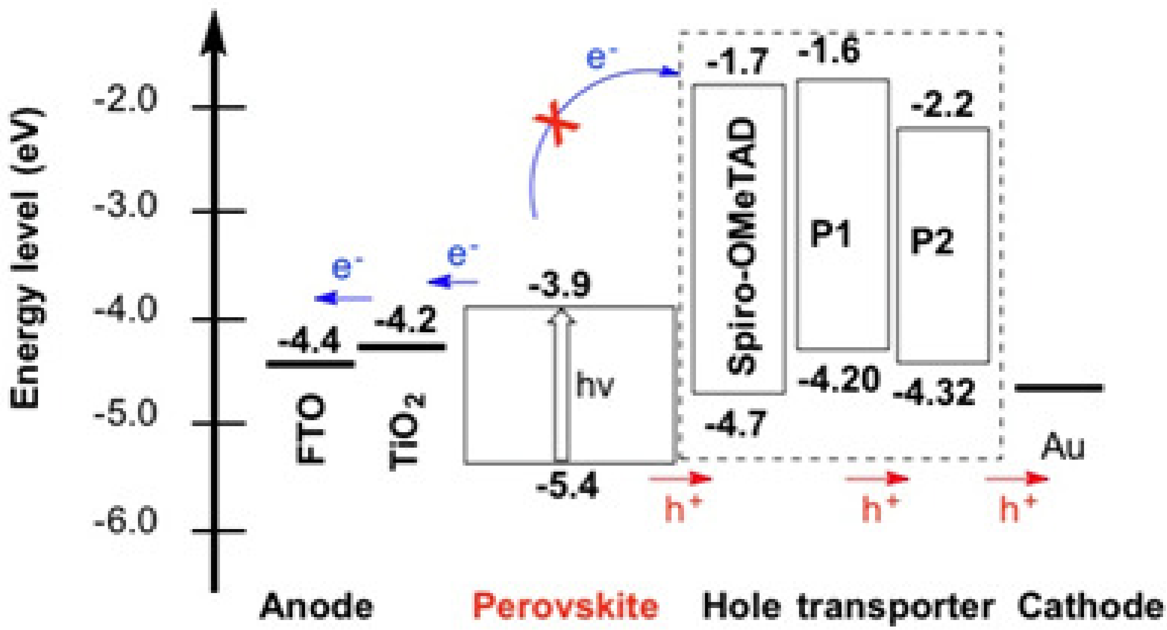


FIGURE 10. Energy level alignment of different device components

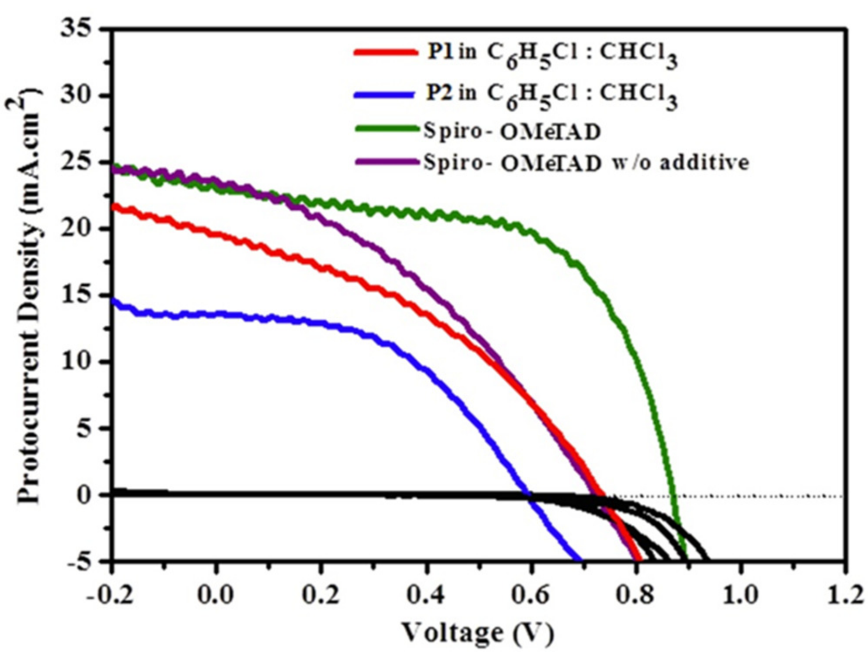


FIGURE 11. J-V curves of P1 (PEDOT·TMeβCD-red) and P2 (PEDOT·TMeγCD-blue).

(**A6**) Electrical properties of PEDOT-TMeβCD, PEDOT-TMeγCD, PEDOT-βCD and PEDOT-γCD

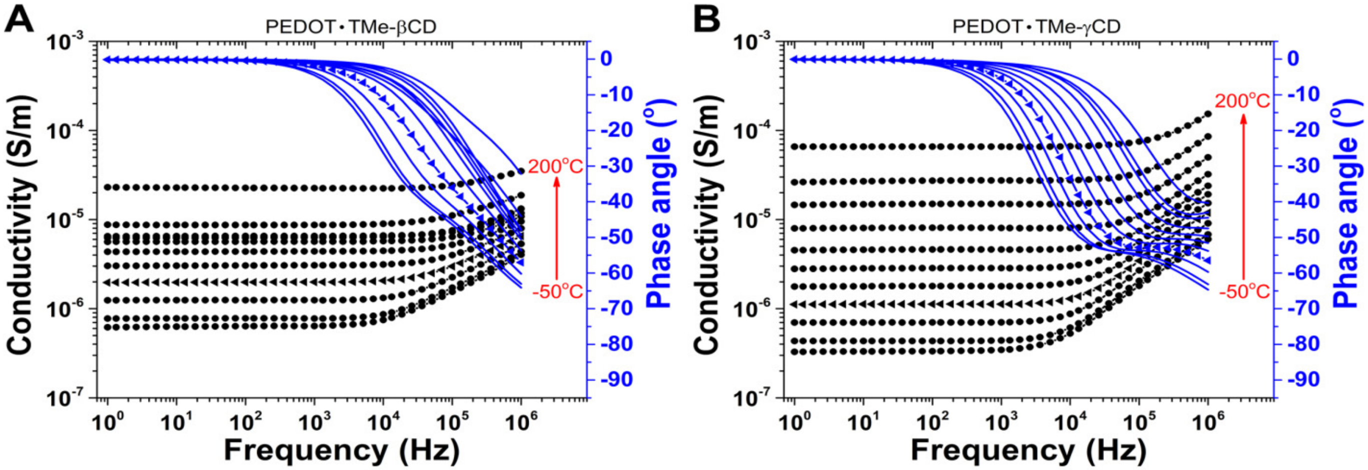


FIGURE 12. The variation of σ and θ with f at different temperatures for PEDOT·TMe-βCD (A) and PEDOT·TMe-γCD (B). Particularly for the temperature of 25 oC, the dielectric spectra are repre-sented with solid triangle-type symbols.

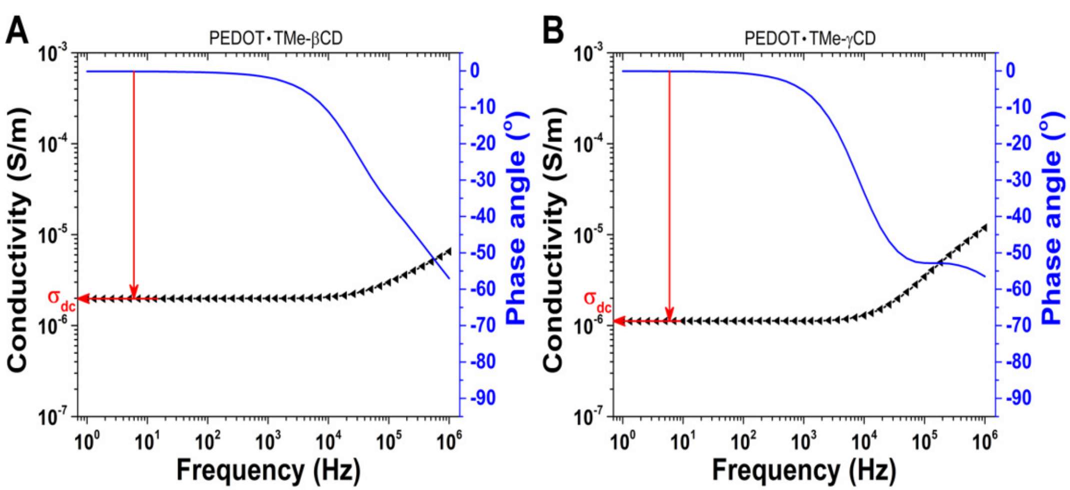


FIGURE 13. The σDC evaluation from the spectrum of PEDOT·TMe-βCD (A) and PEDOT·TMe-γCD (B) at 25 oC. The horizontal arrow illustrates the plateau region of the measured σ, while the vertical arrow shows the maximum value of the θ.

The lowest Ea value of PEDOT·TMe-βCD reveals its better transport of electrons between active sites than those of PEDOT·TMe-γCD.

2D supramolecular organizations at the air-water interface

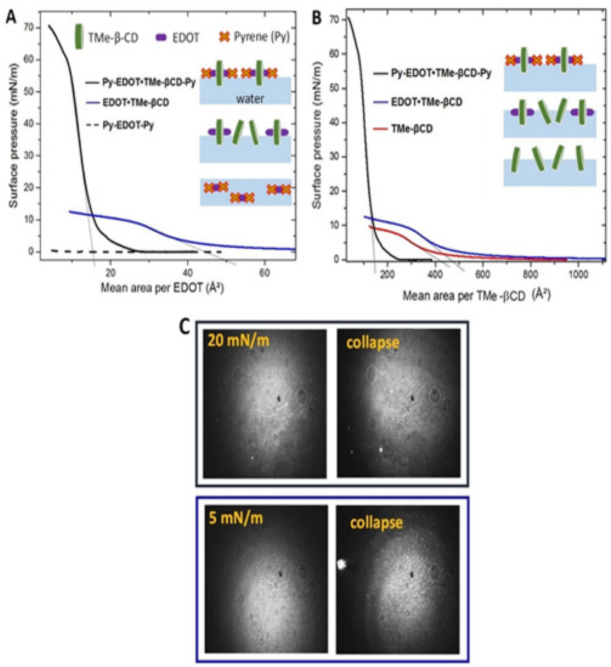


FIGURE 14. Surface pressure–area isotherms for Langmuir films of Py-EDOT·TMe-βCD-Py, EDOT·TMe-βCD and Py-EDOT-Py; (B) Py-TMe-βCD-Py, EDOT·TMe-βCD, and TMe-βCD; (C) BAM images (600 µm × 600 µm) of Py-EDOT·TMe-βCD-Py EDOT·TMe-βCD.

The obtained results strongly suggest that the presence of TMe-CDs on the PEDOT backbones as well the presence of Py ends plays an important role in the supramolecular arrangements of PEDOT·TMe-βCD and PEDOT·TMe-γCD layers.

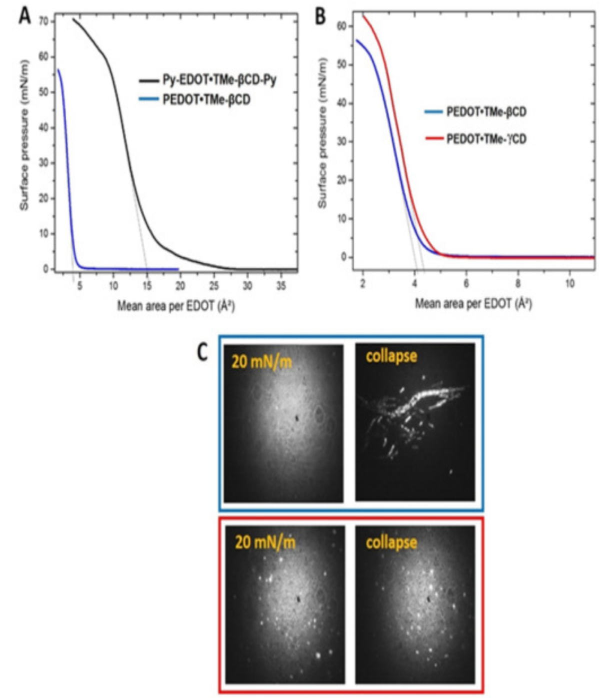
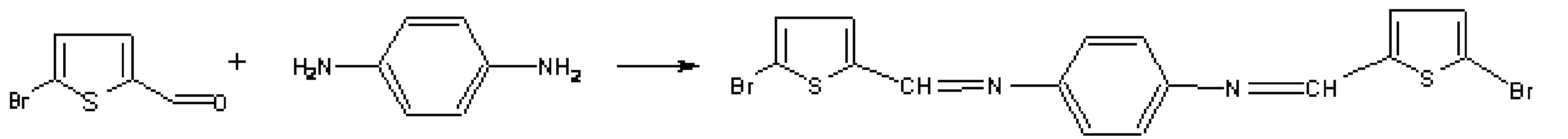


FIGURE 15. Surface pressure-area isotherms presented as a function of the mean area per EDOT monomer for: A) Py-EDOT·TMe-βCD-Py and PEDOT·TMe-βCD; B) PEDOT·TMe-βCD and PEDOT·TMe-γCD and C) BAM images (600 µm x 600 µm) of PEDOT·TMe-βCD and PEDOT·TMeγ-CD Langmuir films in the condensed phase and at the collapse.

(A7) The synthesis and characterization of novel phenylene-thiophene based π-conjugated azomethine (TPA) and its supramolecular complex with permodified β-cyclodextrin



TPA

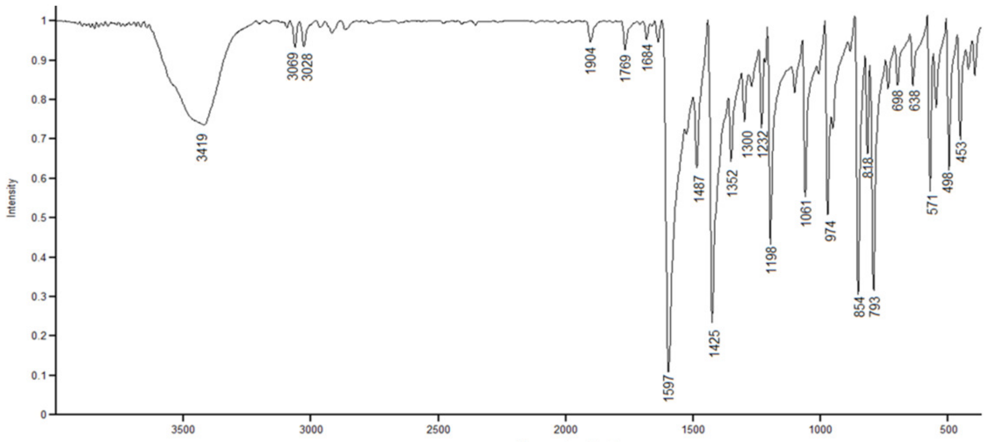


FIGURE 16. FT-IR spectraum of phenylene-thiophene azomethine (**TPA**)

The **TPA** comonomer was synthesized by binding thiophene to the phenylene group

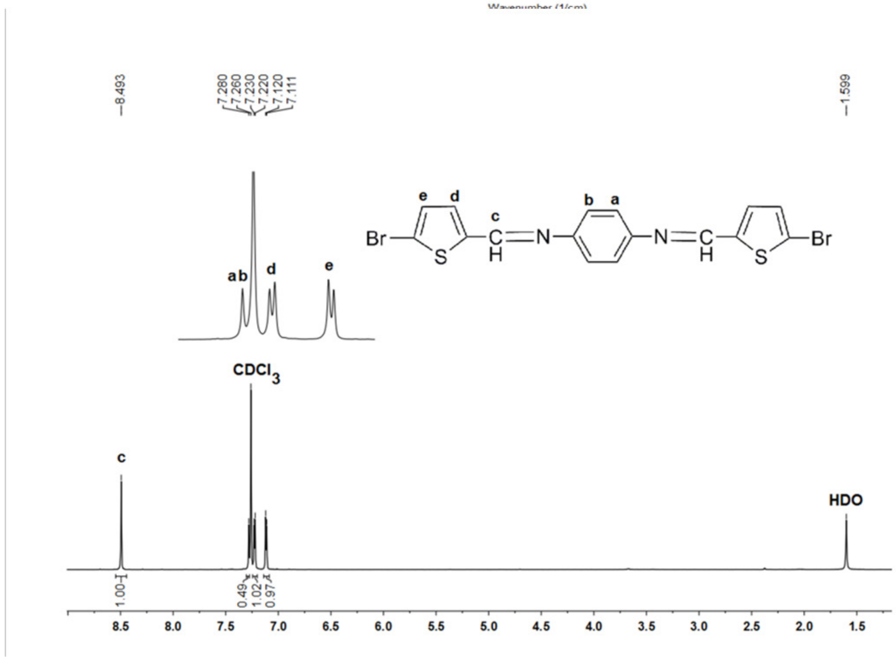


FIGURE 17. 1H-NMR spectrum of phenylene-thiophene azomethine (**TPA**)

Dissemination - 2023

ISI published papers: 5

1. A. Farcaş, A.- M. Resmeriţă, M. Balan-Porcăraşu, C. Cojocaru, C. Peptu, I. Sava, Inclusion complexes of 3,4-ethylenedioxythiophene with permodified β- and γ-cyclodextrins, Molecules, 28, 3404/1-11 (2023) https://doi.org/10.3390/molecules28083404

2. A. Farcaş, M. Damoc, M. Asăndulesa, P.-H. Aubert, R. I. Tigoianu, E. L. Ursu, The straightforward approach of tuning the photoluminescence and electrical properties of encapsulated PEDOT end-capped by pyrene, Journal of Molecular Liquids, 376, 121461/1-10 (2023) https://doi.org/10.1016/j.molliq.2023.121461

3. A. El Haitami, A.-M. Resmeriţă, L. E. Ursu, M. Asăndulesa, S. Cantin, A. Farcaş, Novel insight into the photophysical properties and 2D supramolecular organization of poly(3,4-ethylenedioxythiophene)/permodified cyclodextrins polyrotaxanes at the air water interface, Materials, 16, 4447/1-39 (2023) https://doi.org/10.3390/ma16134757

4. A.-M. Resmeriţă, A. Bargan, C. Cojocaru, A. Farcaş, Synthesis, properties and adsorption kinetic study of new crosslinked composite materials based on polyethylene glycol/polyrotaxane and polyisoprene/semi-rotaxane, Materials, 16, 5594/1-15 (2023) https://doi.org/10.3390/ma16165594

5. D.-A. Blaj, A.-D. Diaconu, V. Harabagiu, C. Peptu, Polyethylene glycol-isophorone diisocyanate polyurethane prepolymers tailored using MALDI MS, Materials, 16, 821/1-16 (2023) https://doi.org/10.3390/ma16020821

Submmited: 1

1. B. Hajduk, A. Farcaş, P. Jarka, H. Bednarski, H. Janeczek, P. Kumari, Spectroscopic ellipsometry investigations and thermal analysis of poly(3,4 ethylenedioxythiophene/cucurbit[7]uril) polypseudorotaxane and polyrotaxane thin films, ACS Macro Letters, mz-2023-00416k

Proceedings ISI: 2

1. M. Asăndulesa, A.-M. Resmeriţă, A. Farcaş, Electrical properties of poly(3,4-ethylenedioxithiophene) threaded by cucurbit[7]uril, Proceedings SPIE, 12493(Advanced Topics in Optoelectronics, Microelectronics and Nanotechnologies XI), 1249304/1-5 (2023)

2. I. R. Tigoianu, A. Farcaş, Photophysical properties of poly(3,4-ethylenedioxythiophene)/permethylated β- and γ- cyclodextrin polyrotaxanes, 10th International Electronic Conference on Sensors and Applications (sciforum-074311) (2023) https://sciforum.net/paper/view/16191

Plenary conferences: 2

1. A. Farcaş, Supramolecular Semiconductor Materials for Organic Electronics, INTERNATIONAL SUMMIT ON POWER AND ENERGY ENGINEERING (ISPEE2023), 23-25.11.2023, Lisbon, Portugal (plenary)

2. A. Farcaş, Cyclodextrins-threaded conjugated polyrotaxanes, an approach to control the intermolecular interactions of organic semiconductors, INTERNATIONAL SUMMIT ON POWER AND ENERGY ENGINEERING (ISPEE2023), 23-25.11.2023, Lisbon, Portugal (Keynote speaker)

International/National Comunications: 4

1. A. Farcaş, Q. Abdelghani, A.-M. Resmeriţă, Cucurbit[7]uril-threaded poly(3,4-ethylenedioxythiophene): A novel processable conjugated pseudopolyrotaxane and polyrotaxane, Advanced Polymers via Macromolecular Engineering (APME2023), 23-27.04.2023, Paris-France

2. A. Farcaş, A.-M. Resmeriţă, Supramolecular organization of poly(3,4-ethylenedioxythiophene)/permodified cyclodextrins polyrotaxanes on the 2D Materials, The 7th European Cyclodextrin Conference (EuroCD2023), 05-08.09.2023, Budapest-Hungary

3. A.-M. Resmeriţă, A. Farcaş, Freestanding composites material films obtained by cross-linking of polyethylene glycol polyrotaxane and polyisoprene/semi-rotaxane with 2-hydroxypropyl-β-cyclodextrins, The 7th European Cyclodextrin Conference (EuroCD2023), 05-08.09.2023, Budapest-Hungary
4. M. Balan-Porcăraşu, A. Farcaş, Insights into the inclusion complexation of 3,4-ethylenedioxyrhiophene with permodified cyclodextrins in aqueous solution, Progress in organic and macromolecular compounds (MACRO IASI), 29th edition, 04.-06.10.2023, Iaşi, România

International Posters: 3
I. R. Tigoianu, A. Farcaş, Photophysical properties of poly(3,4-ethylenedioxythiophene)/permethylated β- and γ- cyclodextrin polyrotaxanes, 10th International Electronic Conference on Sensors and Applications (sciforum-074311) , 15.11.2023 (online)
2. M. Asăndulesa, A.-M. Resmeriţă, A. Farcaş, Electrical properties of poly(3,4-ethylenedioxythiophene)/permodified cyclodextrins polyrotaxanes end-capped by pyrene, Materials, Methods & Technologies 2023, 25th International Conference, 17-20.08.2023, Burgas-Bulgaria
3. B. Hajduk, A. Farcaş, P. Jarka, H. Janeczek, Thermal properties of soluble poly(3,4 ethylenedioxythiophene/cucurbit[7]uril) polypseudorotaxane and polyrotaxane, Polskie Towarzystwo Kalorymetrii, 15-16.02.2023, Gdańsk, Politechnika Gdańska Wydział Chemiczny, Poland

Other:

1. A. Farcaş - Program Committee, KEYNOTE and Plenary SPEAKER at the International Summit on Power and Energy Engineering (ISPEE2023), 23-25.11. 2023, Lisbon, Portugal

2. A. Farcaş - Topic Editor in Frontiers in Physics in the Research Topic "Physical Properties of Materials for Organic Optics and Optoelectronics"

3. Chair for the Semiconductors and Optoelectronics Forum 12-14 august 2024/Madrid-Spain

4. Certificate of Recognition and Appreciation for the contribution as a plenary speaker at International Summit on Power and Energy Engineering (ISPEE 2023)

5. Certificate of Recognition and Appreciation for the contribution as a keynote speaker at International Summit on Power and Energy Engineering (ISPEE 2023)