



CNCS



SUPRAMOLECULAR ORGANIC SEMICONDUCTING MATERIALS FOR OPTOELECTRONICS

Acronim: SUPRAMOL-MAT

Scientific Report STAGE 2 / 2023

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PROJECT MANAGER

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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-TMe β CD, PEDOT-TMe γ CD, PEDOT- β CD and PEDOT- γ CD and their physical characterizations;

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

(A3) Evaluation of PEDOT-TMe β CD, PEDOT-TMe γ CD, PEDOT- β CD and PEDOT- γ CD photophysical properties;

(A4) Electrochemical properties of PEDOT-TMe β CD, PEDOT-TMe γ CD, PEDOT- β CD and PEDOT- γ CD;

(A5) The photovoltaic performance of the devices based on PEDOT-TMe β CD and PEDOT-TMe γ CD;

(A6) Electrical properties of PEDOT-TMe β CD, PEDOT-TMe γ CD, PEDOT- β CD and PEDOT- γ CD;

(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 permethylated or native cyclodextrins

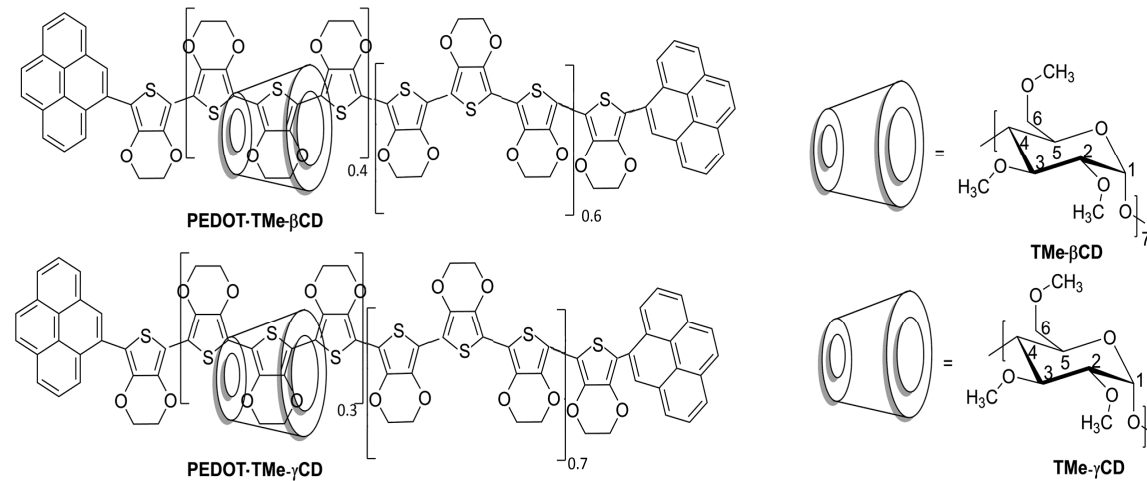


FIGURE 1. Chemical structures of PEDOT-TMe-βCD and PEDOT-TMe-γCD

O3 - 2023

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

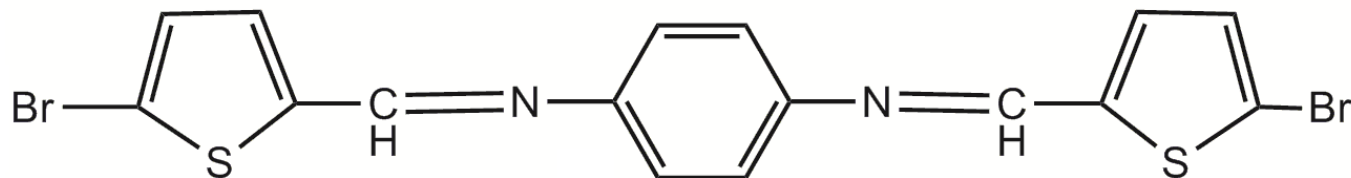


FIGURE 2. Chemical structure of TPA comonomer

(A1) Synthesis of PEDOT-TMe β CD, PEDOT-TMe γ CD, PEDOT- β CD and PEDOT- γ CD and their chemical characterizations

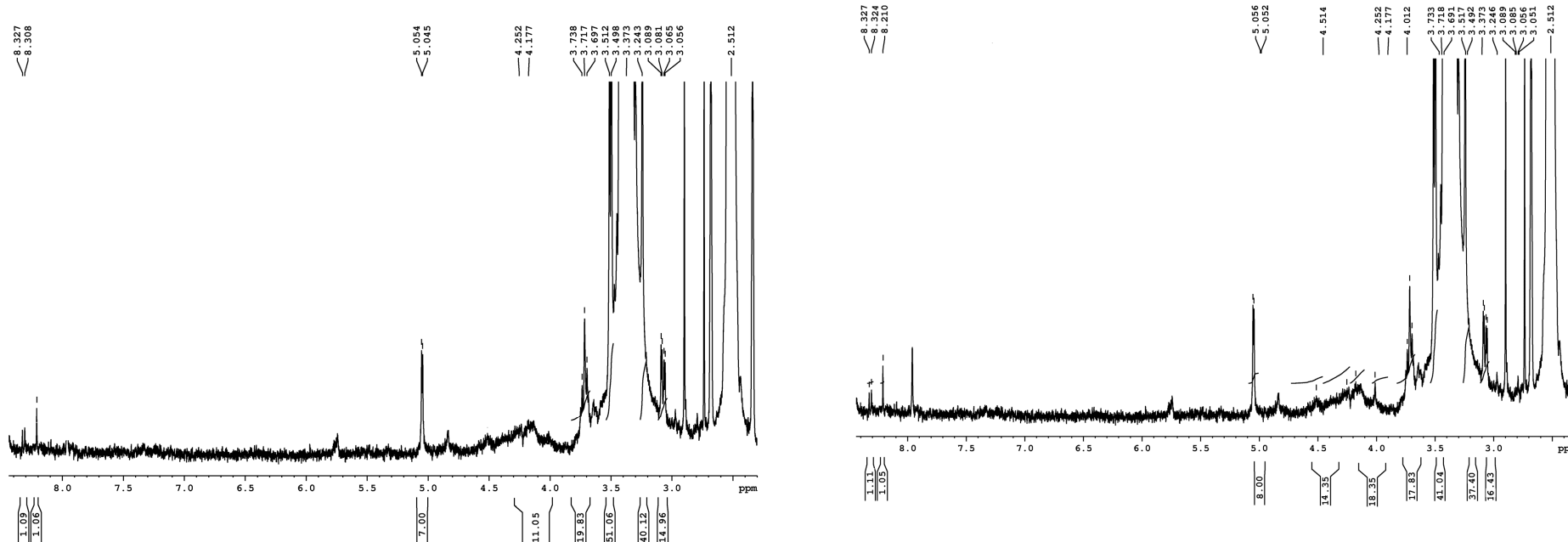


FIGURE 3. ¹H-NMR spectra of PEDOT·TMe- β CD (left) and PEDOT·TMe- γ CD (right).

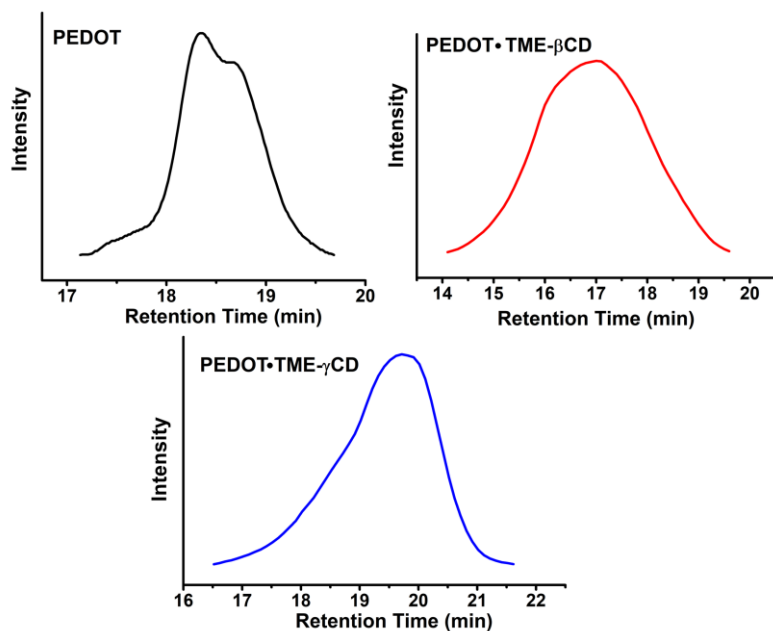


FIGURE 4. Comparison between the chromatograms of PEDOT, PEDOT·TMe- β CD and PEDOT·TMe- γ CD.

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

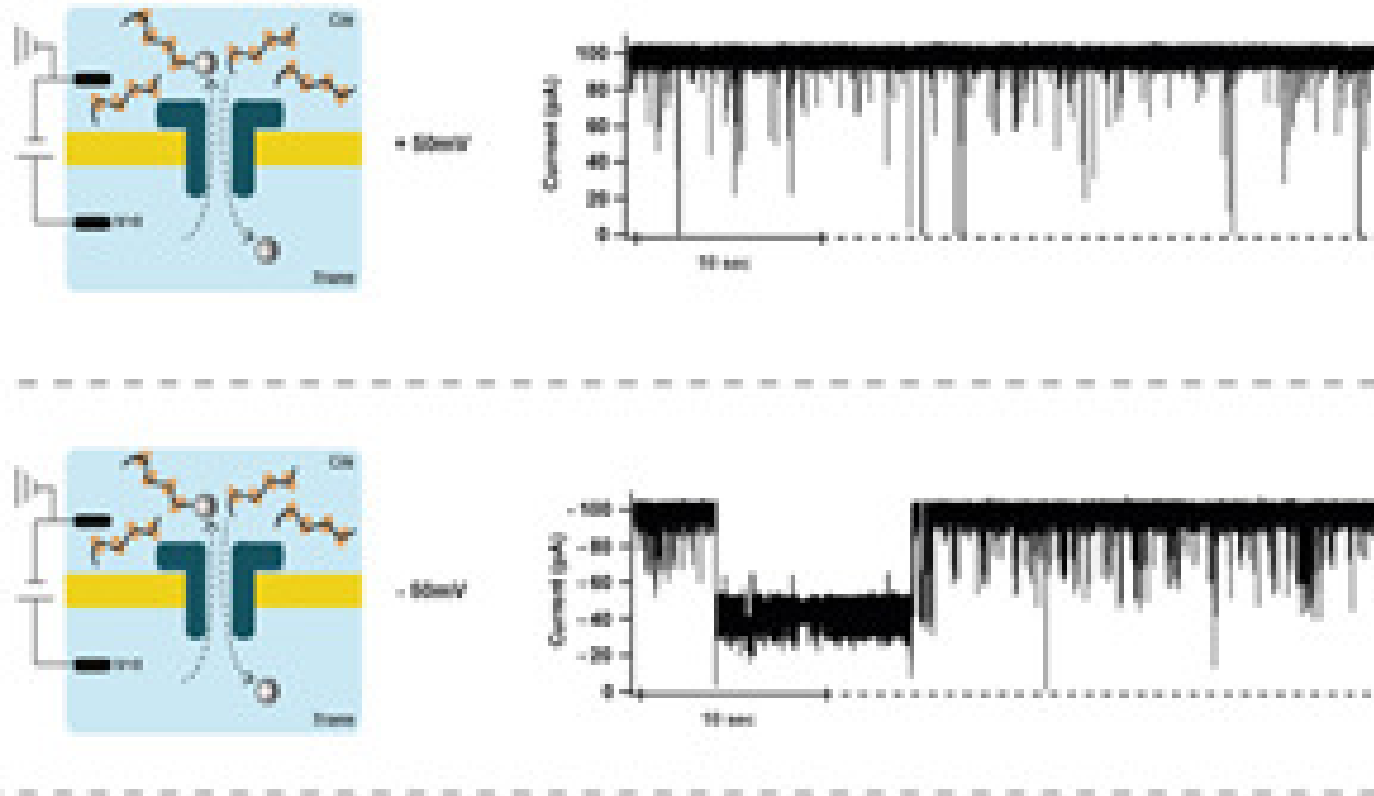


FIGURE 5. Electrical detection of PEDOT-TMe- β CD PR using the AeL nanopore. Illustration of the experimental setup used for the analysis of the PEDOT-CB7-PPs molecules added in the cis compartment in the presence of an AeL nanopore inserted in a lipid bilayer. Portions of a typical current traces recorded in the presence of 0.6 mM PEDOT-TMe- β CD 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- β CD compounds to the pore lumen of AeL at a single molecule level.

(A3) Photophysical properties of PEDOT-TMe β CD, PEDOT-TMe γ CD, PEDOT- β CD and PEDOT- γ CD

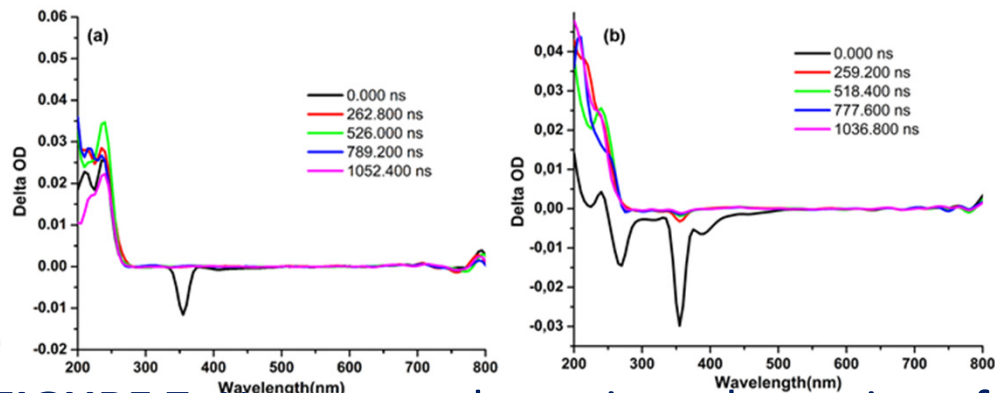
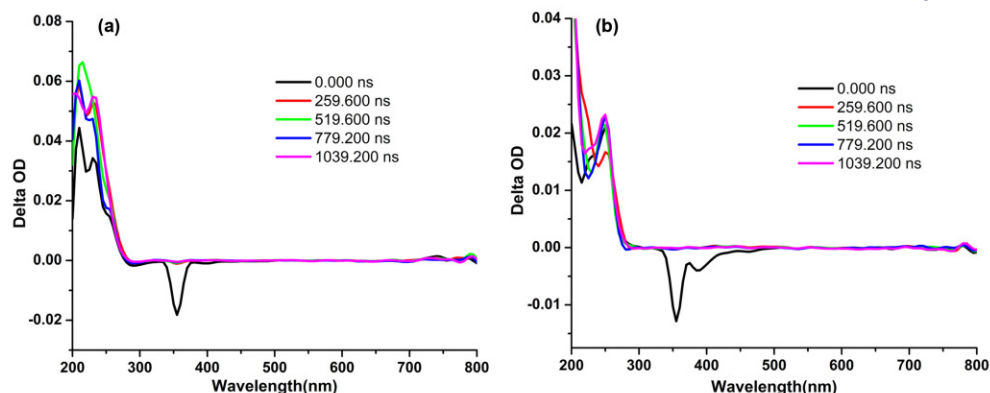


FIGURE 6. Nanosecond transient absorption of PEDOT-TMe- β CD in H₂O (λ_{ex} = 375 nm) (a) and ACN (λ_{ex} = 355 nm) (b).

FIGURE 7. Nanosecond transient absorption of PEDOT-TMe- γ CD in H₂O (λ_{ex} = 375 nm) (a) and ACN (λ_{ex} = 355 nm) (b)

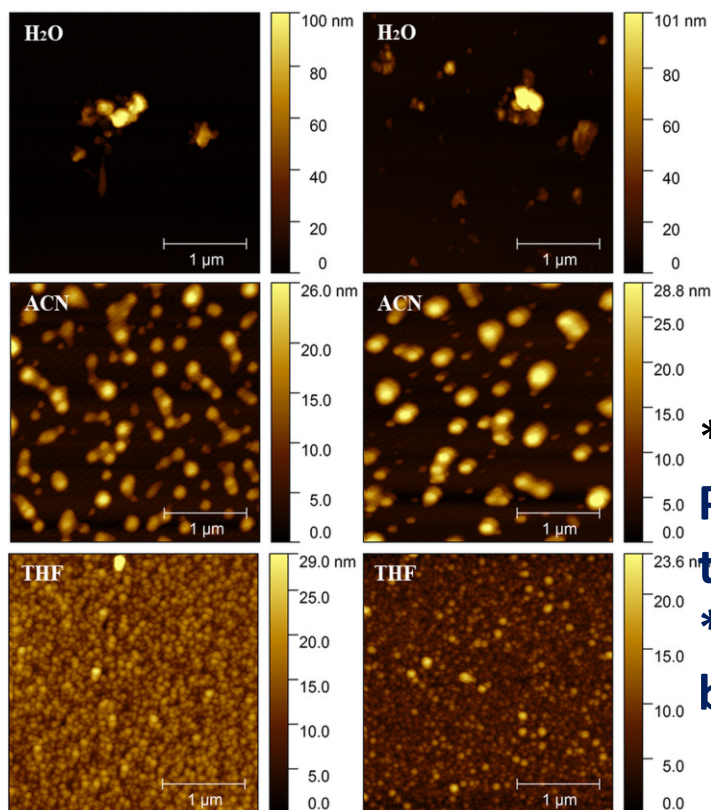


FIGURE 8. The AFM surface morphology over area of $3 \times 3 \mu\text{m}^2$ of PEDOT-TMe- β CD (left) and PEDOT-TMe- γ CD (right) films obtained by drop casting from H₂O, ACN and THF.

*The optical results indicated that PEDOT-TMe- β CD and PEDOT-TMe- γ CD are sensitive to the polarity changes of the microenvironment.

*These encapsulated PEDOT compounds exhibited better Φ_{FL} and Φ_{PH} efficiencies in ACN than in H₂O.

(A4) Electrochemical properties of PEDOT-TMe β CD, PEDOT-TMe γ CD, PEDOT- β CD and PEDOT- γ CD

Cyclic voltammograms of PEDOT-TMe- β CD and PEDOT-TMe- γ CD

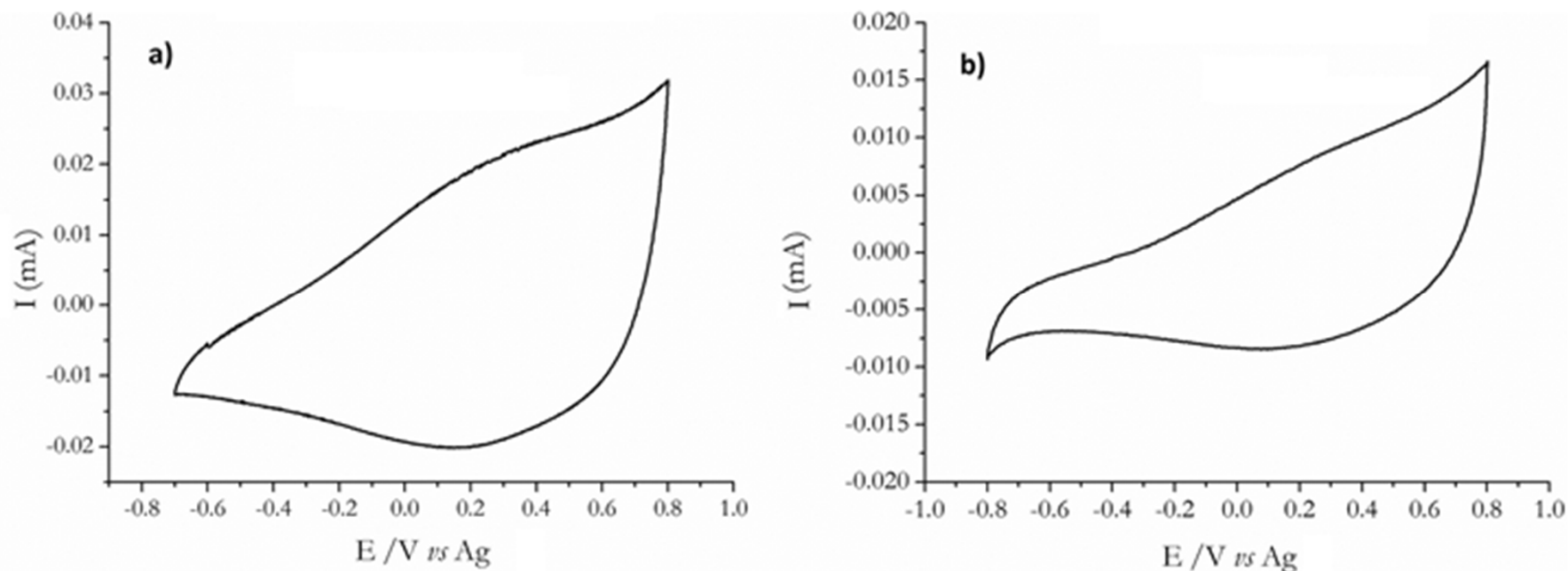


FIGURE 9. CV of PEDOT-TMe- β CD (a) and PEDOT-TMe- γ CD (b) in 0.1 M TBAClO₄/ACN solution at scan rate 20 mV·s⁻¹.

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

(A5) Preliminary photovoltaic results of PEDOT-TMeβCD and PEDOT-TMeyCD

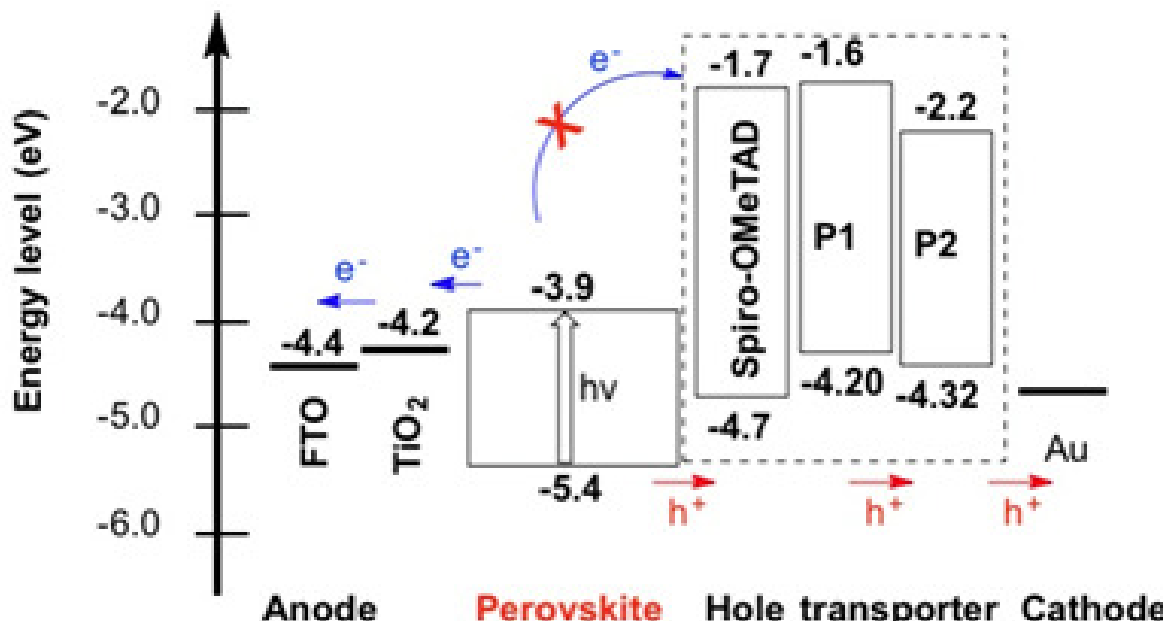


FIGURE 10. Energy level alignment of different device components

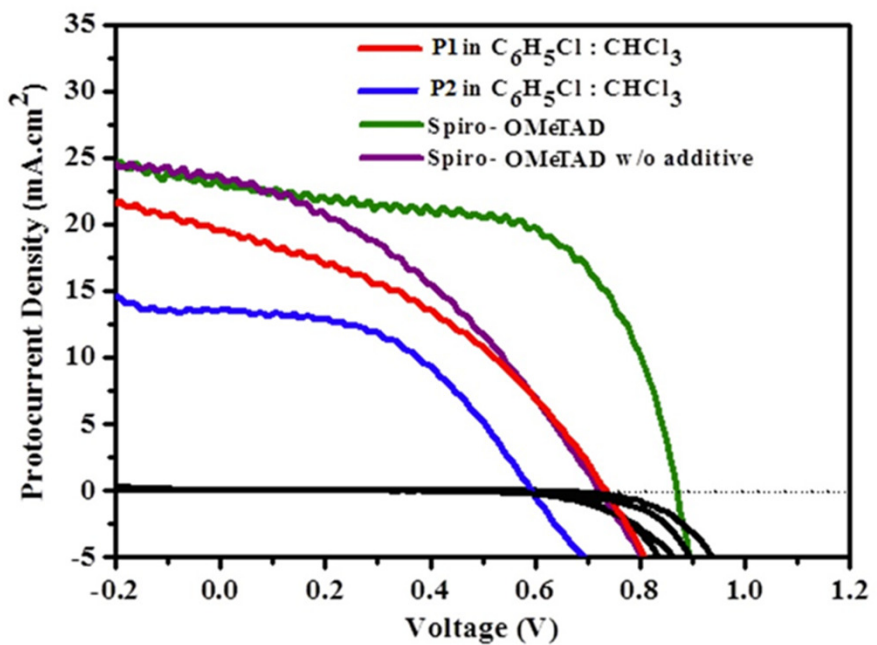


FIGURE 11. J-V curves of P1 (PEDOT·TMeβCD-red) and P2 (PEDOT·TMeyCD-blue).

(A6) Electrical properties of PEDOT-TMe β CD, PEDOT-TMe γ CD, PEDOT- β CD and PEDOT- γ CD

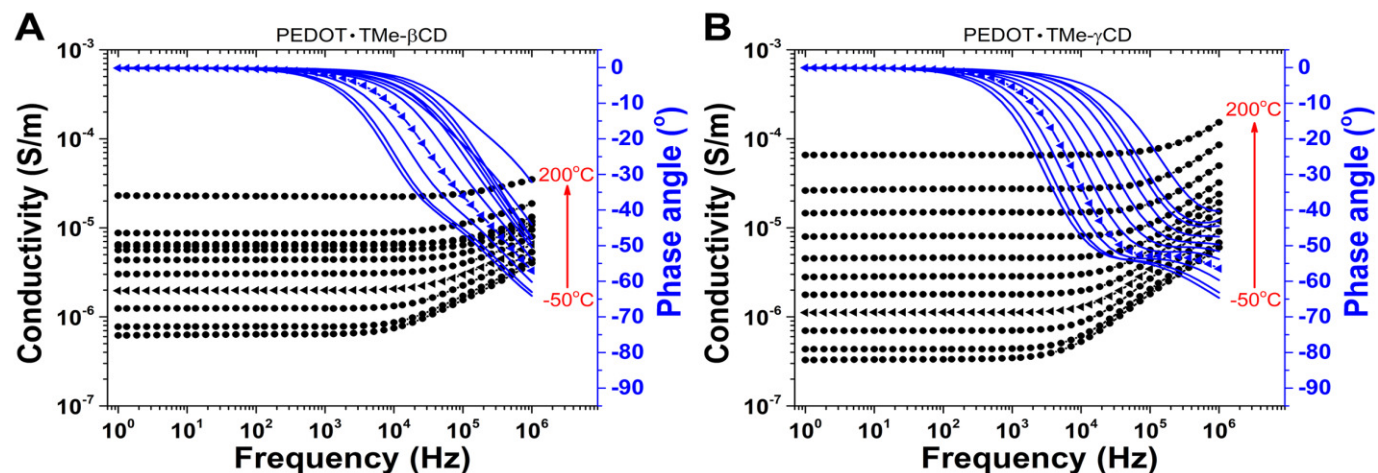


FIGURE 12. The variation of σ and θ with f at different temperatures for PEDOT·TMe- β CD (A) and PEDOT·TMe- γ CD (B). Particularly for the temperature of 25 oC, the dielectric spectra are represented with solid triangle-type symbols.

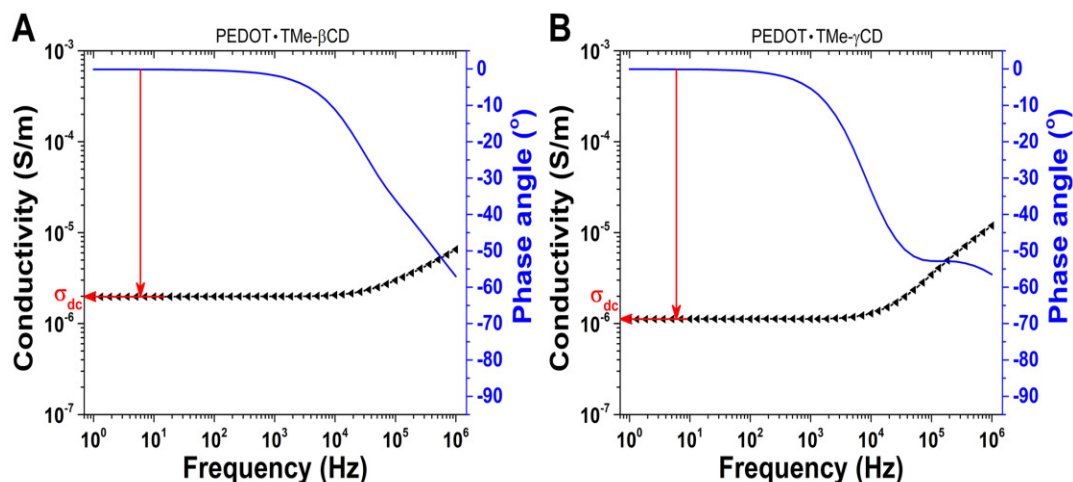


FIGURE 13. The σ_{DC} evaluation from the spectrum of PEDOT·TMe- β CD (A) and PEDOT·TMe- γ CD (B) at 25 oC. The horizontal arrow illustrates the plateau region of the measured σ , while the vertical arrow shows the maximum value of the θ .

The lowest E_a value of PEDOT·TMe- β CD reveals its better transport of electrons between active sites than those of PEDOT·TMe- γ CD.

2D supramolecular organizations at the air-water interface

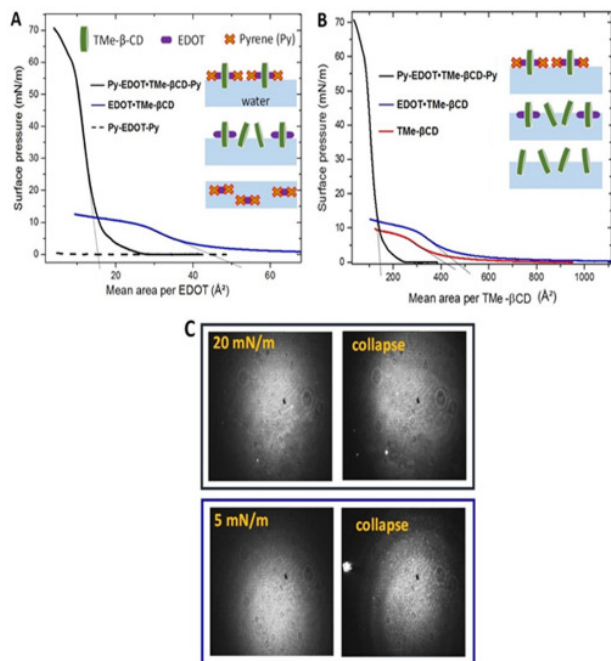


FIGURE 14. Surface pressure–area isotherms for Langmuir films of Py-EDOT·TMe-βCD-Py, EDOT·TMe-βCD and Py-EDOT-Py; (B) Py-TMe-βCD-Py, EDOT·TMe-βCD, and TMe-βCD; (C) BAM images (600 μm × 600 μm) of Py-EDOT·TMe-βCD-Py EDOT·TMe-βCD.

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.

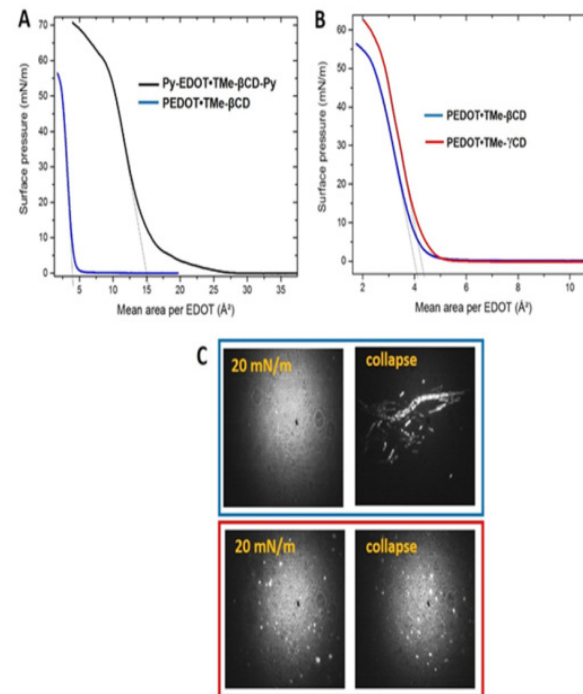
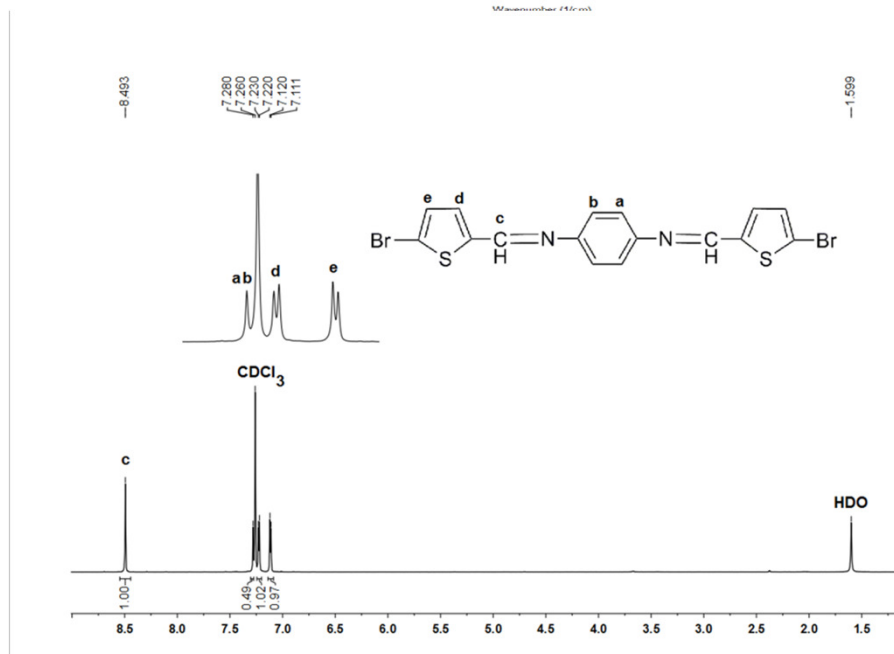
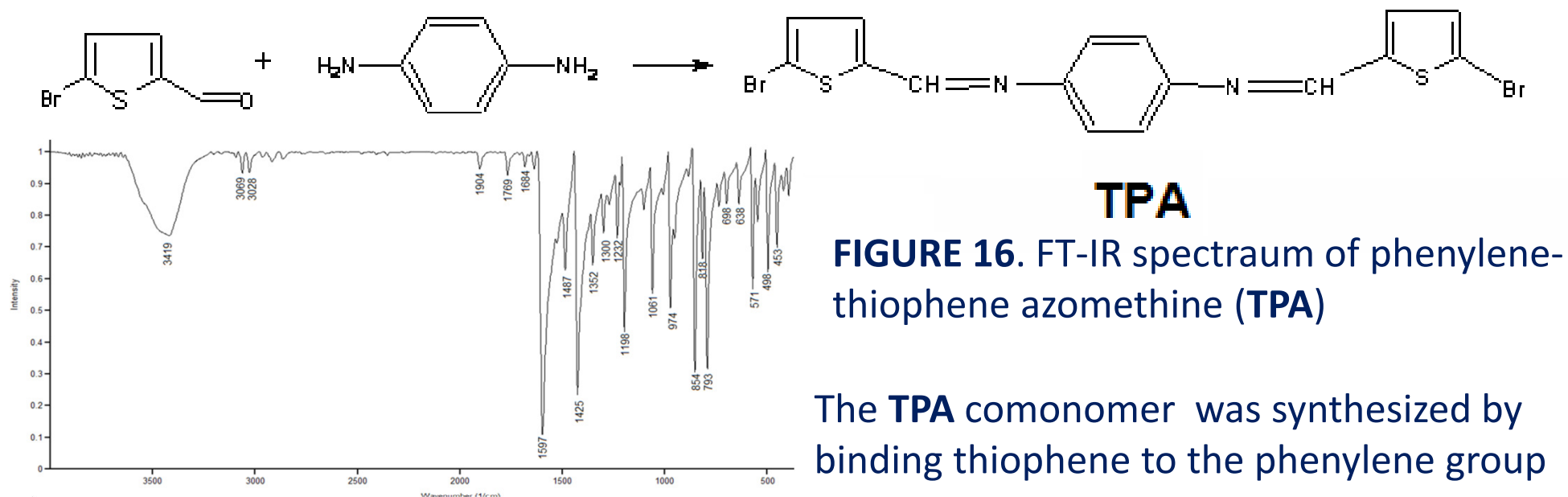


FIGURE 15. Surface pressure–area isotherms presented as a function of the mean area per EDOT monomer for: A) Py-EDOT·TMe-βCD-Py and PEDOT·TMe-βCD; B) PEDOT·TMe-βCD and PEDOT·TMe-γCD and C) BAM images (600 μm × 600 μm) of PEDOT·TMe-βCD and PEDOT·TMe-γCD Langmuir films in the condensed phase and at the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

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



Dissemination - 2023

Published papers in ISI journal

1. A. Farcas, H. Ouldali, C. Cojocaru, M. Pastoriza-Gallego, A.-M. Resmerita, A. Oukhaled
Structural characteristics and the label-free detection of poly(3,4-ethylenedioxythiophene/cucurbit[7]uril) pseudorotaxane at single molecule level, *Nano Research*, 16, 2728- 2737 (2023)
2. A. Farcas, A.- M. Resmerita, M. Balan-Porcarasu, C. Cojocaru, C. Peptu, I. Sava
Inclusion complexes of 3,4-ethylenedioxythiophene with permodified β - and γ -cyclodextrins , *Molecules*, 28, 3404/1-11 (2023)
3. A. Farcas, M. Damoc, M. Asandulesa, 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)
4. A. El Haitami, A.-M. Resmerita, L. E. Ursu, M. Asandulesa, S. Cantin, A.Farcas
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)

5. A.-M. Resmerita, A. Bargan, C. Cojocaru, A. Farcas

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)

6. M. Asandulesa, A.-M. Resmerita, A. Farcas

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

International conferences

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

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. Farcas, A.-M. Resmerita

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. Resmerita, A. Farcas

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

5. A. Farcas

Supramolecular Semiconductor Materials for Organic Electronics

INTERNATIONAL SUMMIT ON POWER AND ENERGY ENGINEERING (ISPEE2023), 23-

25.11.2023, Lisabona, Portugalia

6. M. Balan-Porcarasu, A. Farcas

INSIGHTS INTO THE INCLUSION COMPLEXATION OF 3,4-ETHYLENEDIOXYTHIOPHENE WITH PERMODIFIED CYCLODEXTRINS IN AQUEOUS SOLUTION

Progress in organic and macromolecular compounds 29th edition, 04.-06.10.2023, Iasi, Romania

Poster at international conferences

1. I. R. Tigoianu, A. Farcas

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. Asandulesa, A.-M. Resmerita, A. Farcas

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