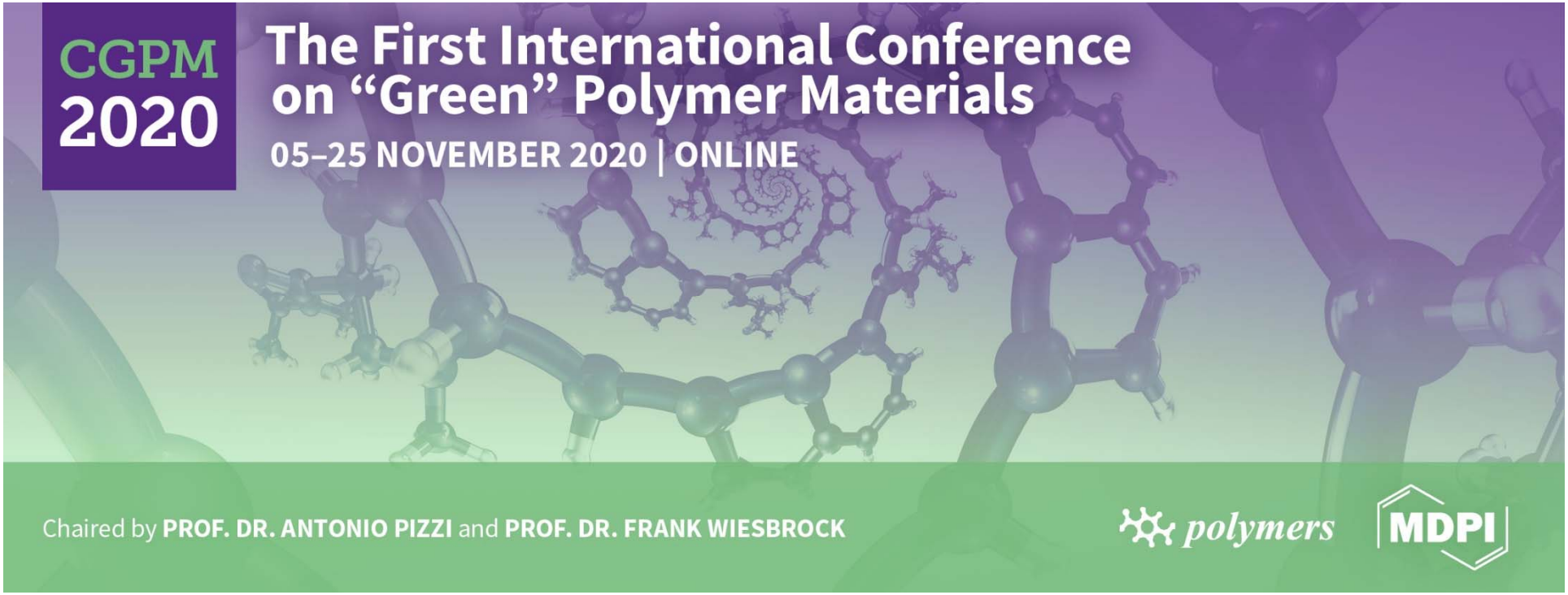
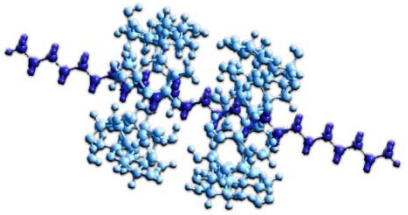


Anca-Dana Bendrea[1,*], Luminita Cianga[1], Gabriela-Liliana Ailiesei[1], and Ioan Cianga[1*]

[1] "Petru Poni" Institute of Macromolecular Chemistry, 41 A Grigore-Ghica Voda Alley, Iasi, RomaniaAffiliation, Address;

- anca.bendrea@icmpp.ro; ioanc@icmpp.ro

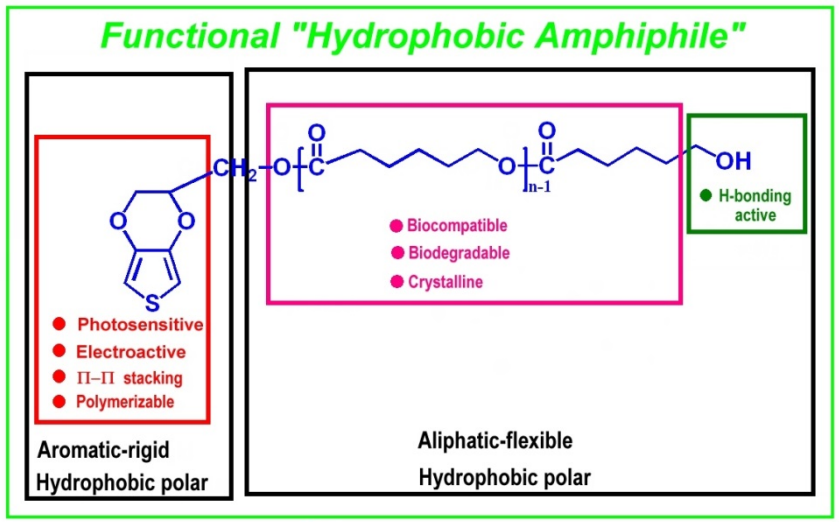


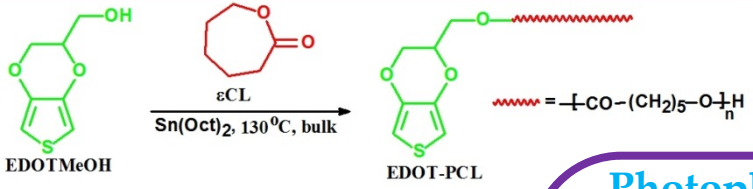
Fluorescent EDOT-functionalized poly-ε-caprolactone: Synthesis, photophysical and self-assembling properties in organic solvents and its serendipitously noticed behaviour in protonated media

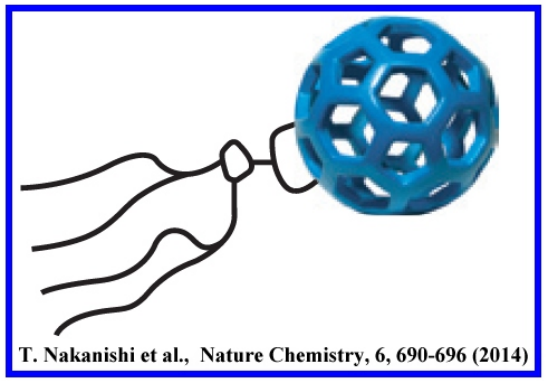
In the last few years several fluorescent poly-ε- caprolactones [1-3] were designed, synthesized and subsequently used as nanoparticles [1], nanofibers [2] or scaffolds [3] in various prospective bioapplications. Meanwhile, our interest was directed toward electro - and photoactive moieties - functionalized poly/or oligo-ε- caprolactone, that worked as key building blocks (macromonomers) for new grafted conjugated polymers or hybrid systems successfully used as biosensors [4,5] or regenerative medicine [6]. In the same line, the present report is aimed to extend the investigations and to highlight the properties in solution (photophysical, self-assembling) of 3, 4-ethylenedioxythiophene-functionalized poly-ε- caprolactone (EDOT-PCL) synthesized by ring-opening polymerization (ROP). The results of the studies in two organic solvents (chloroform and acetonitrile), having different selectivity in relation with the constitutive parts of EDOT-PCL, revealed its propensity for self-assembling, proved by Dynamic Light Scattering (DLS) measurements, while fluorescent emission maxima in the range 310-430 nm, depending on the solvent were evidenced, as well. Moreover, its capability for spontaneous oxidant-free oligomerization, presumably due to and under the action of acidic character of $CDCl_3$, serendipitously noticed during ^{13}C-NMR registration, was subsequently validated by experiments performed in chloroform in the presence of hydrochloric acid. This is an interesting and applications-oriented useful observation which supports that recently demonstration of oxidant-free polymerization of common EDOT in the only presence of some organic acids [7] could also be extended to EDOT-containing more complex structure.

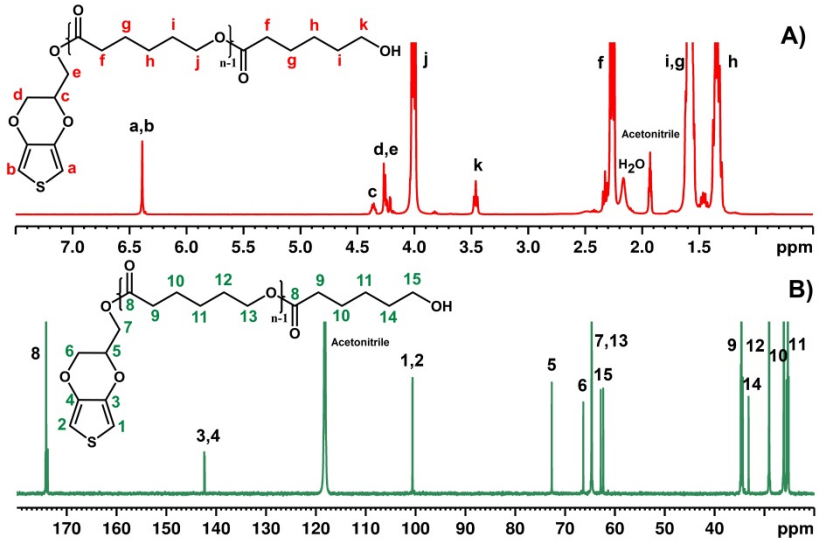
1. Huang,S., Liu, S., Wang, K., Yang,C. Luo, Y., Zhang,Y., Cao, B., Kang, Y., Wang, M., Nanoscale, 2015,7, 889-895.
2. H .J. Diao, K.Wang, H. Y. Long, M. Wang, S.Y. Chew, Adv. Healthcare Mater., 2016, 5, 529–533.
3. S. Huang, K. Wang, S. Wang, Y. Wang, M. Wang, Adv. Mater. Interfaces, 2016, 1600259.
4. B. G. Molina, A. D. Bendrea, L. Cianga, E. Armelin, Luis J. del Valle, I. Cianga, C. Alemán, Polym. Chem., 2017, 8, 6112–6122.
5. B. G. Molina, L. Cianga, A.D. Bendrea, I. Cianga, C. Alemán, E. Armelin, Polym. Chem., 2019, 10, 5010–5022.
6. B. G. Molina, A. D. Bendrea, S. Lanzalaco, L. Franco, L. Cianga, L. J. del Valle, J. Puiggali, P. Turon, E. Armelin, I. Cianga, C. Aleman, J. Mater Chem B, 2020, doi.org/10.1039/D0TB01259A
7. E. Tomšík, I. Ivanko, J. Svoboda, I.Šeděnková, A. Zhigunov, J. Hromádková, J. Pánek, M. Lukešová, N. Velychkivska, L. Janisová, Macromol. Chem. Phys. 2020, 2000219

Results and Discussion



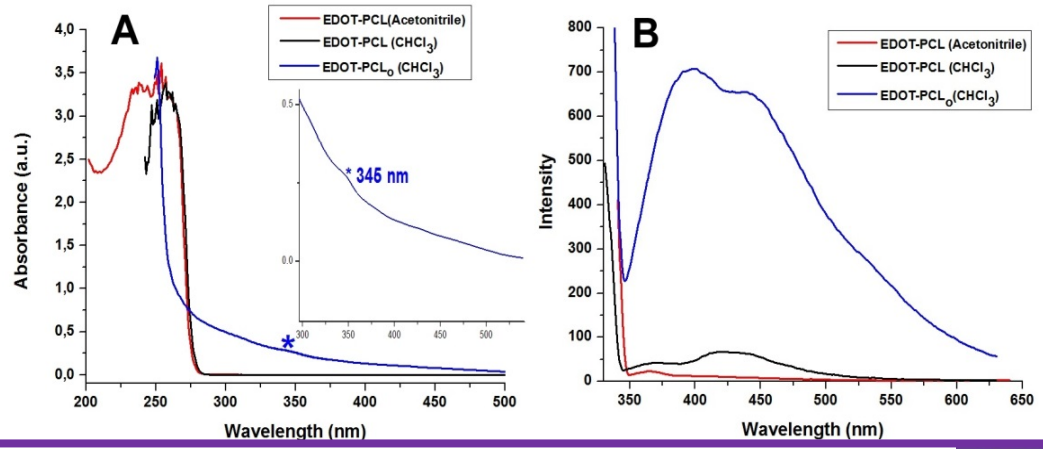






^{1}H (a) and ^{13}C (b) NMR spectra of EDOT-PCL macromonomer in CD_3CN

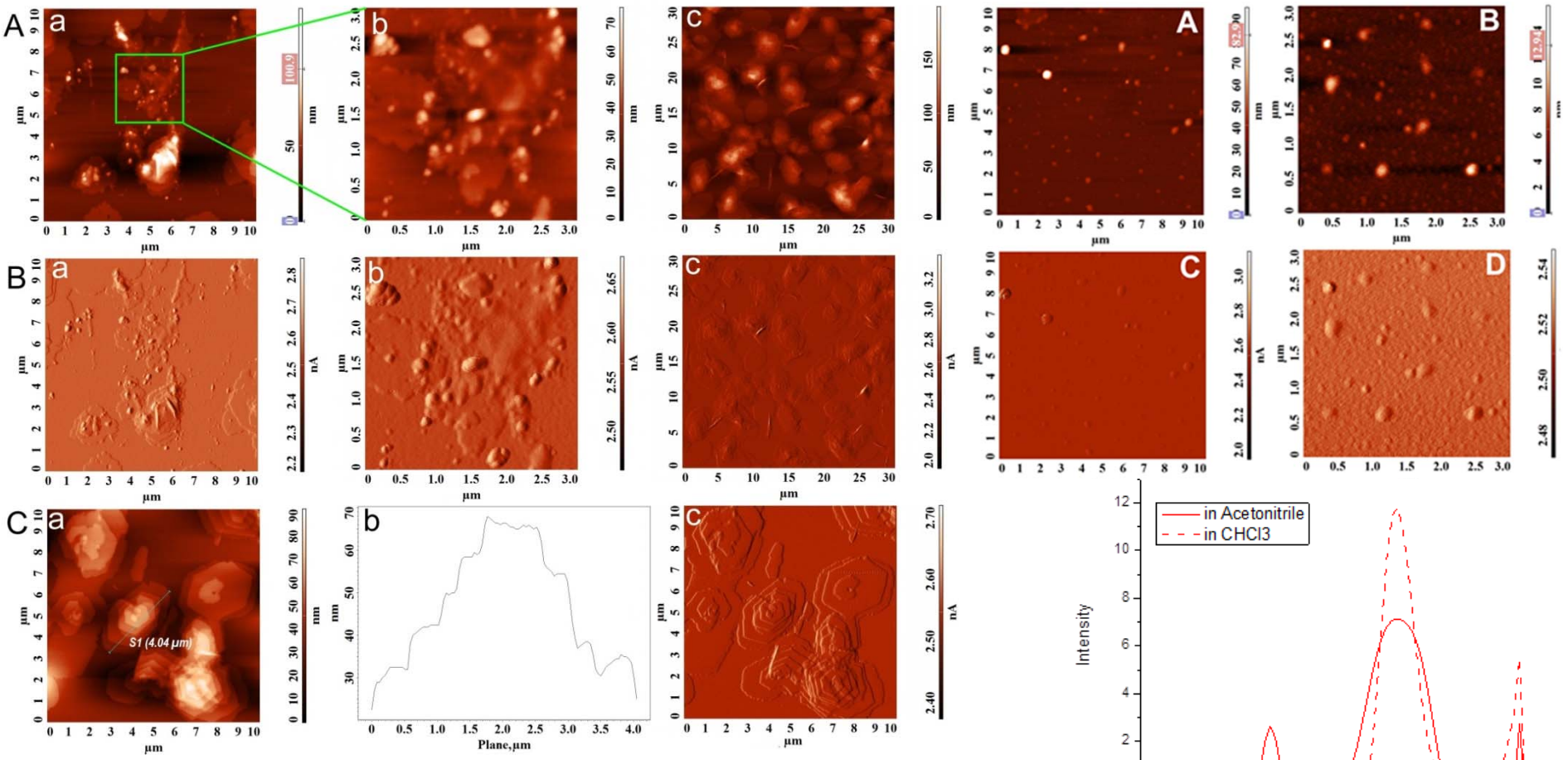
Photophysical Properties of the investigated compounds



! PCL works as an electronic shield which preserve and protect the fluorescence of EDOT.

The morphology of EDOT-PCL in thin films obtained by drop-casting method from a solution of 1mg/ml in

Acetonitrile **and** **Chloroform**

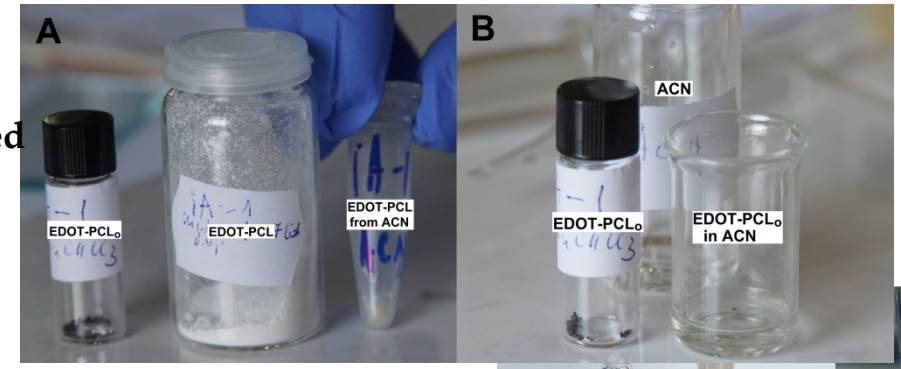


✓ **By changing solvent selectivity toward either part of EDOT-PCL, which are mutually immiscible and with geometric and energetic mismatch, EDOT-PCL self-assembles into supramolecular structures with distinct shapes and sizes.**

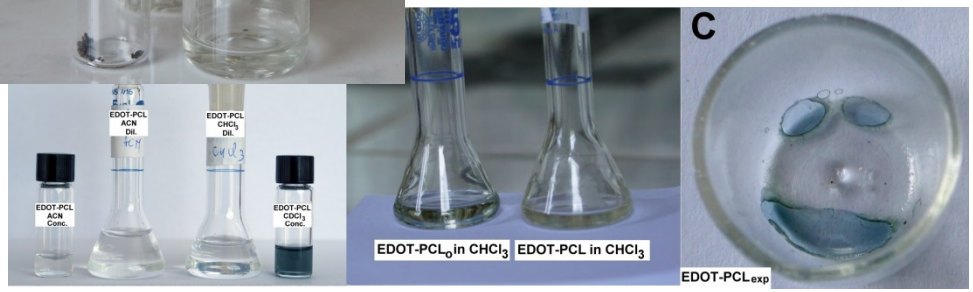
CGPM 2020

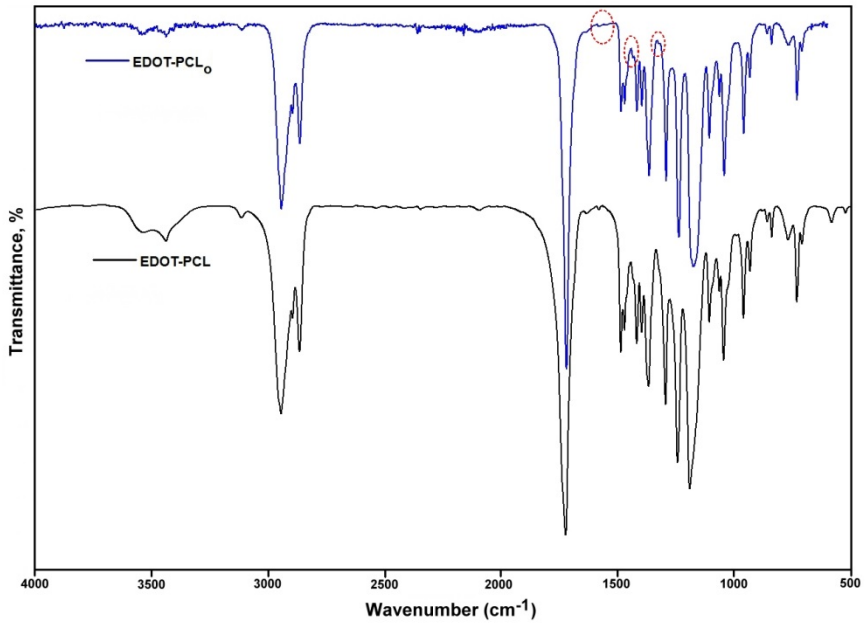
EDOT-PCL behaviour in the presence of acids

A)- The bulk form of EDOT-PCL as resulted from the reaction, of EDOT-PCL as resulted after evaporation of an ACN solution and EDOT-PCL oligomerized form (EDOT-PCL$_o$), as resulted after evaporation of acidic $CDCl_3$ solution

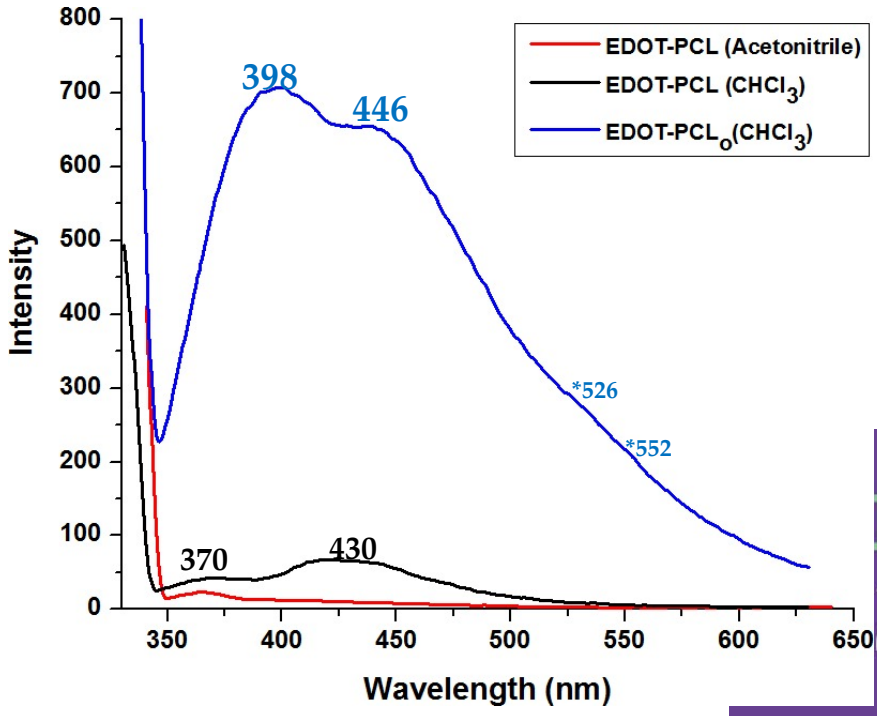


(B)- Photo showing the colourless, transparent aspect of EDOT-PCL$_o$ ACN solution that show a blue colour when is solved in chloroform





FT-IR spectra of **EDOT-PCL** and **EDOT-PCL$_o$**



PM 20

Conclusions

- ✓ A π-conjugated molecule- EDOT-PCL- constructed solely of hydrophobic domains, able to show an interaction-based bias in organic solvents was designed and synthesized.
- ✓ The experimental results showed that, in solvents with extreme different polarity, EDOT-PCL present a bias strong and selective enough to exert control over supramolecular packing conducting to a diversity of self-assembled structures as shape and size (globular, helical rods, orthorhombic single crystals and 3D spiral structures).
- ✓ The self-assembling of EDOT-PCL is balanced by the mismatch between aromatic-aliphatic and rigid-flexible character of its structural building elements, being assisted by the solute-solute and/or solute-solvent weak non-covalent interactions (solvophobic - solvophilic, hydrogen bonding, π-π interactions).
- ✓ The self-assembled supramolecular structures are fluorescent with an enhanced intensity in less polar chloroform solvent, PCL preserving the fluorescence of EDOT moiety.
- ✓ In the presence of inorganic clorhidric acid EDOT-PCL macromonomer oligomerization was noticed and proved as well, this finding showing promises for the oxidant-free polymerization toward an useful biocompatible and more sustainable conjugated PEDOT polymer.

Acknowledgments

The authors acknowledges the financial support of a grant of Ministry of Research and Innovation, CNCS-UEFISCDI, Project number PN-III-P4-ID-PCCF-2016-0050, Acronym 5D-nanoP.

CGPM 2020