ELECTROCHEMICAL POLYMERIZATION OF CARBAZOLE DERIVATIVES

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Introduction

• Conjugated microporous polymers (CMPs) have been synthesized via oxidative coupling polymerization of multifunctional monomers, showing high surface area and high operational stability [1-2]. However, they have been mostly prepared as intractable powders. For a couple of potential applications, the generation of thin films of CMPs is necessary but a challenging issue. Electrochemical polymerization (EP) of suitable monomers allows a controlled deposition of thin and smooth films which have been recently shown as promising materials in applications such as explosive's sensors [3] and organic photovoltaic devices (OPVs) [4].

• In this work, 4,4'-bis(N-carbazolyl)-1,1'-byphenyl (CBP), 4,7-bis(4-(9H-carbazol-9-yl)phenyl)benzo[c][1,2,5]thiadiazole (CBPBT), 4,4',4''-tri-9-carbazolyl-triphenylamine (CTPA) and 1,3,5-tris(N-carbazolyl)benzene (TCB) were polymerized using potentiodynamic EP in order to produce thin and smooth films. Electrochemical, optical and morphological characterization were carried out for all the four deposits.

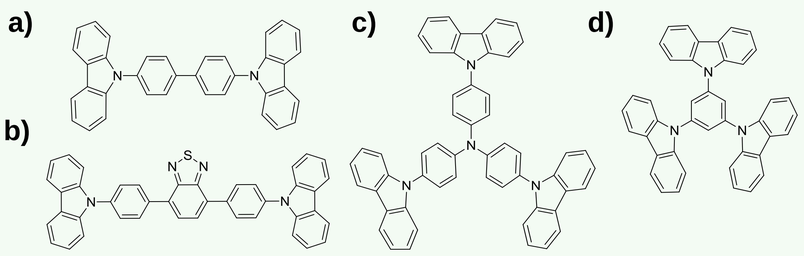


Fig 1. Chemical structures of a) CBP, b) CBPBT, c) CTPA, and d) TCB

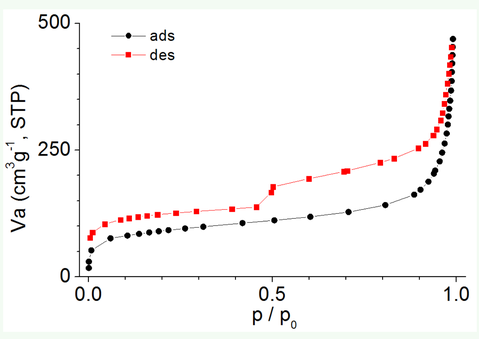


Fig 2. N_2 isotherm of PCBPBT at 77 K. PCBPBT was obtained as a bulk polymer via oxidative coupling (*vide infra*).

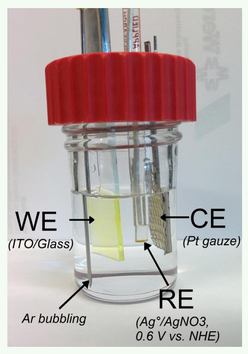


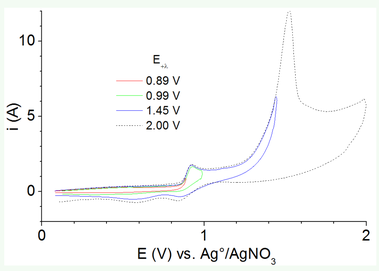
Fig 3. Three-electrodes cell used by us for EP.

Experimental Section

2 mM Mon / 0.1 M TBAP in MeCN:DCM (1:1), under Ar atm at 25 °C (5 mL).

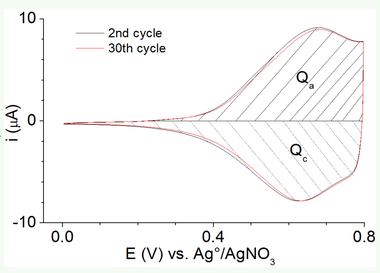
WE: Pt (A = 0.008 cm²)

Electrochemical characterization



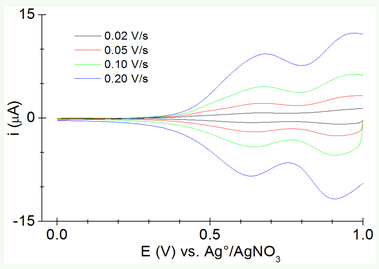
Potential range of EP

• 1st voltammetric cycle from 0 V to different values of the oxidative switching potential ($E_{+\lambda}$) for the EP of CBPBT. The sweeping rate was 0.1 V/s.



Stability and reversibility of the deposit

• 2nd and 30th voltammetric cycles (0 - 0.8 V) of a PCBPBT deposit in a monomer–free solution. The sweeping rate was 0.2 V/s.

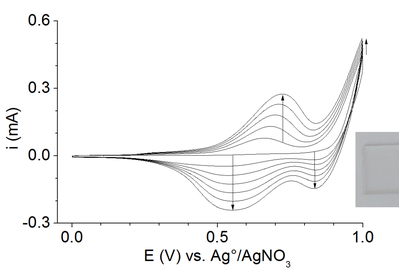


Adherence and electrical contact of the deposit with the electrode

• 2nd voltammetric cycle (0 - 1 V) of a PCBPBT deposit in a monomer-free solution. The sweeping rate was varied between 0.02 and 0.20 V/s

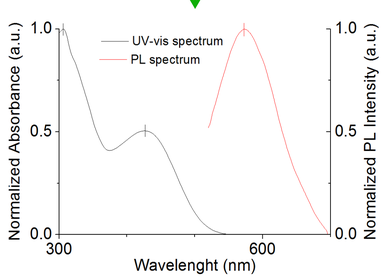
0.5 mM Mon / 0.1 M TBAP in MeCN:DCM (1:4), under Ar atm at 25 °C (10 mL).

Potentiodynamic EP (6 cycles, 0 →$E_{+\lambda}$)

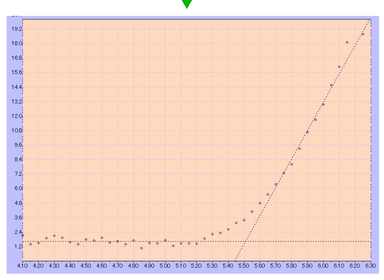


WE: ITO (A = 2.5 cm²)

Film Characterization

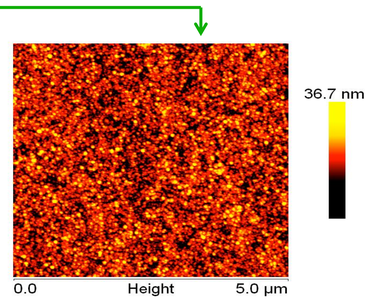


• UV-vis and PL spectra of a thin film of PCBPBT on ITO.



• AC-2 plot for determination of the HOMO level of a thin film of PCBPBT on ITO.

• Profilometry scan of a thin film of PCBPBT on ITO.



• Contact-mode AFM surface image of a thin film of PCBPBT on ITO (topology).

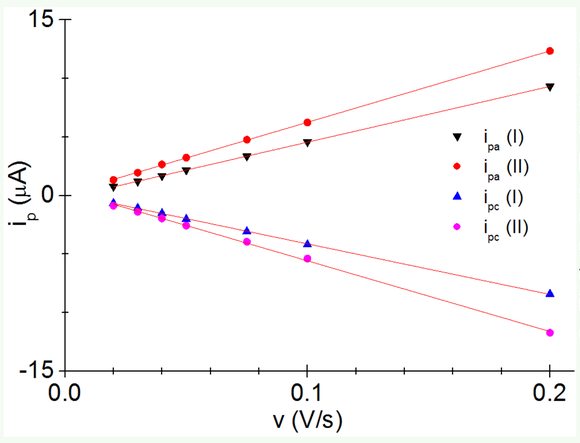
Results

• For CBPBT polymerization the anodic switching potential ($E_{+\lambda}$) can be changed in a broad range (0.91 - 1.51 V), in order to have the EP of CBPBT as the main reaction.

Fig 3. Dependence of the ratio of reduction (Q_{red}) and polymerization charge (Q_{pol}) on the value of anodic switching potential ($E_{+\lambda}$) that is applied in the first cycle during EP of CBPBT.

• The ratio between anodic (Q_a) and cathodic (Q_c) charge reflects the reversibility of the charging process of a deposit under the mentioned conditions. A value close to 1 demonstrates reversibility of the charging process of the polymer.

Fig 4. Relationship of anodic and cathodic charge (Q_a and Q_c) and the number of cycles for a PCBPBT film on ITO in a monomer-free sol. The applied potential range was 0 - 0.8 V with a sweeping rate of 0.1 V/s.



• The linear dependence between i_p and v is characteristic of an electroactive polymer that is well-adhered on the electrode with the current originating from the PCBPBT film which is localized on the electrode surface.

Fig 5. Dependence of the anodic and cathodic current peaks (i_{pa} and i_{pc}) on the sweeping rate (v) for a PCBPBT film on ITO in a monomer-free sol. The potential range was 0 - 1 V.

Table 1. Electrochemical, optical and morphological data for EP of carbazole derivatives monomers and the resulting deposits.

Monomer	CBP	CBPBT	CTPA	TCB
Range of EP (V)	0.90 - 1.55	0.91 - 1.51	1.18 - 1.50	0.95 - 1.70
E_g (eV)	3.42	2.72	3.37	2.72
HOMO (eV)	5.70	5.51	5.54	5.67
LUMO (eV) [a]	2.28	2.79	2.17	2.95
λ_{max} A (nm)	350	305, 425	333	301, 380
λ_{max} PL (nm)	449	571	437	453
Thickness (nm)	114	66	98	56
rRMS (nm)	15	15	31	4
Surface area [b] (m^2/g)	671 [c]	324 [d]	1065 [d]	2220 [c]

[a] Obtained from the difference between optical band gap (E_g) and HOMO energy.
[b] Measured for bulk polymers made by oxidative coupling conditions.
[c] From the references 3 and 4.
[d] 6 eq $FeCl_3$, 24 h, r.t.

Conclusions

• Multifunctional carbazole-based monomers have been successfully polymerized using potentiodynamic electrochemical polymerization.
•Promising electrochemical properties are shown for the four different deposits.
•The optical and morphological properties of the thin films of conjugated microporous polymers based on carbazole make them good candidates for applications as sensors or as interlayers in OPVs.
•Next step will be a direct measurement of the surface area of the electrochemically generated films.

Acknowledgment

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References

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