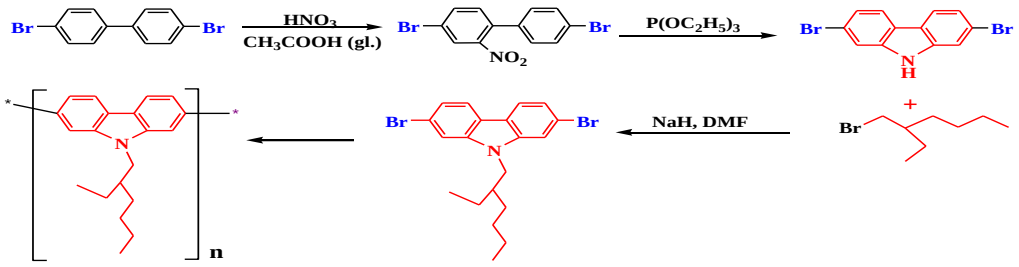
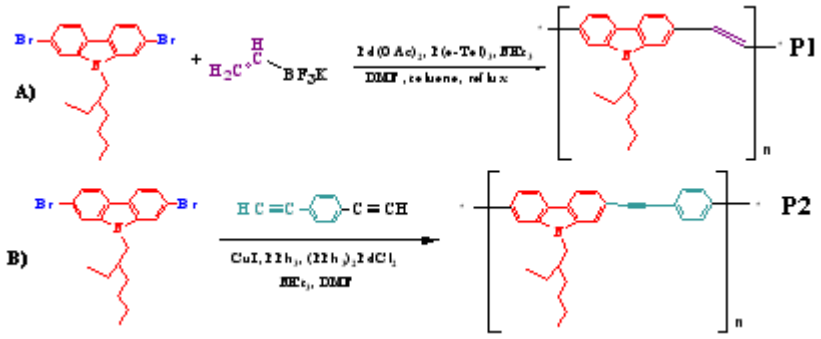
## RESULTS 2012

**Objectives**

1. **Synthesis of new conjugated polymer structures**
2. **Synthesis and characterization of star and dendrimer oligomers**
3. **New acceptor compounds**




***Scheme 1:*** *Synthesis of 2,7-dibromo N-(2-etyl hexyl) carbazole*




***Scheme 2:*** *Synthesis of arylene vinylene (P1) and arylene ethynylene (P2) polymers containing 2.7-carbazolildiyl groups.*

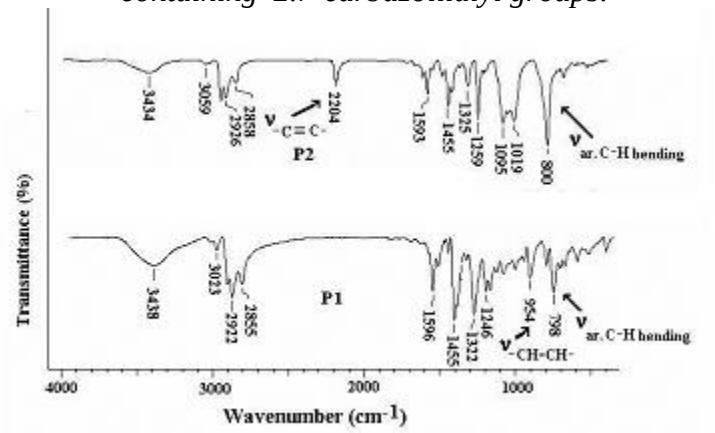



***Figure 1:*** *FT-IR spectra (KBr pellet) of polymers* ***P1-P2***

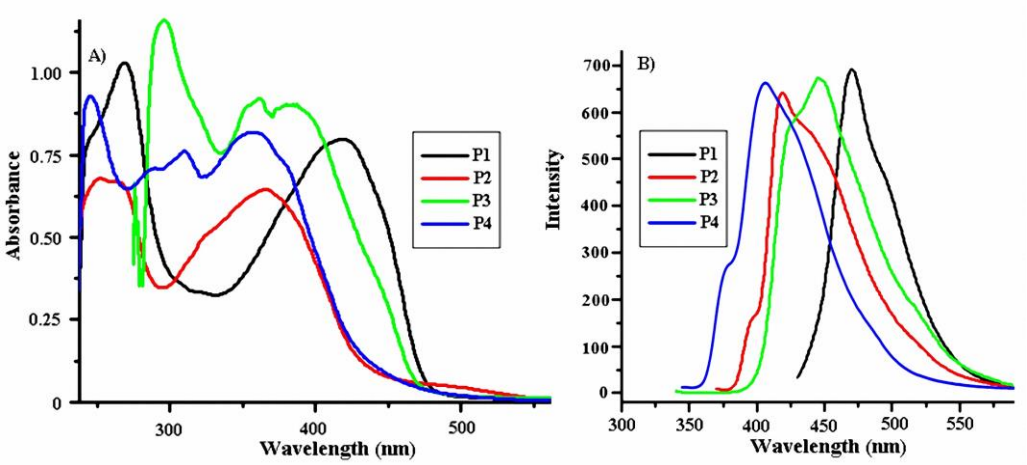



***Figure 2:*** *Absorption (A) and emission (B) spectra ($CHCl_3$) of polymers P1-and P2. P3 and P4 are polymers containing 3,6 carbazolediyl groups*

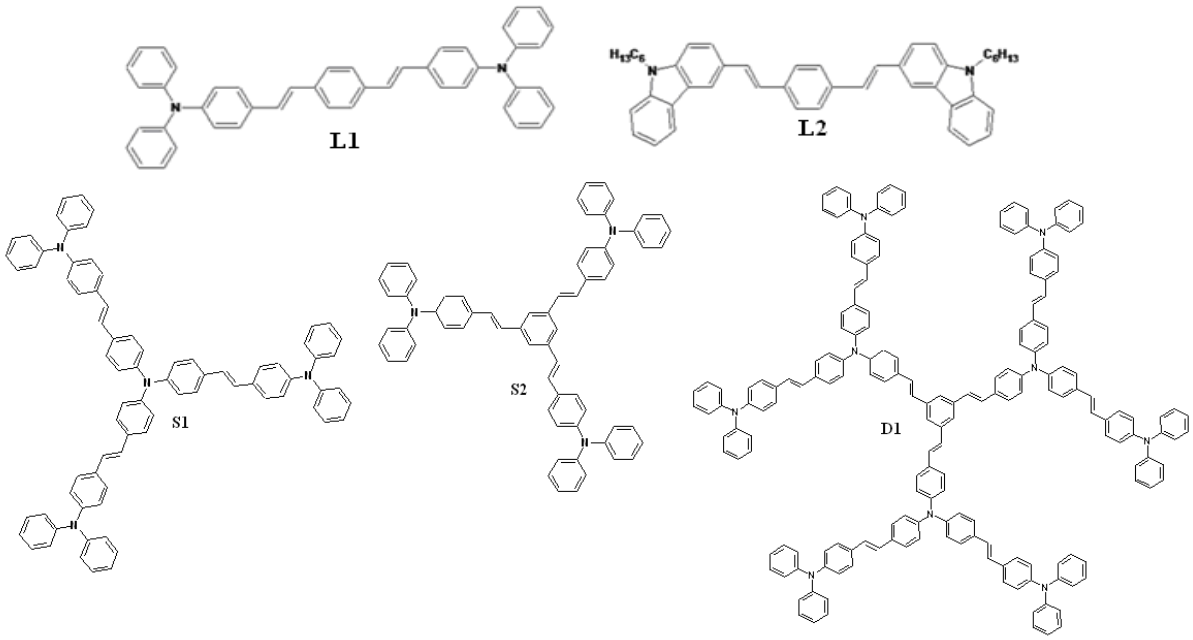
***Table 1:*** *Electrochemical characteristics of polymers*

| Polymer | $\lambda_{abs}^{max}$ (nm) | $\lambda_{em}^{max}$ (nm) | $E_{ox}^{onset}$ (V) *vs* Ag/AgCl | $E_{red}^{onset}$ (V) *vs* Ag/AgCl | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) | $E_g$ (eV) |
|---|---|---|---|---|---|---|---|
| P1 | 271, 414 | 469 | 0,97 | 1.0 | -5.31 | -3,34 | 1,97 |
| **P2** | 251, 370 | 421 | 0,92 | 1.21 | -5.26 | -3,13 | 2,13 |

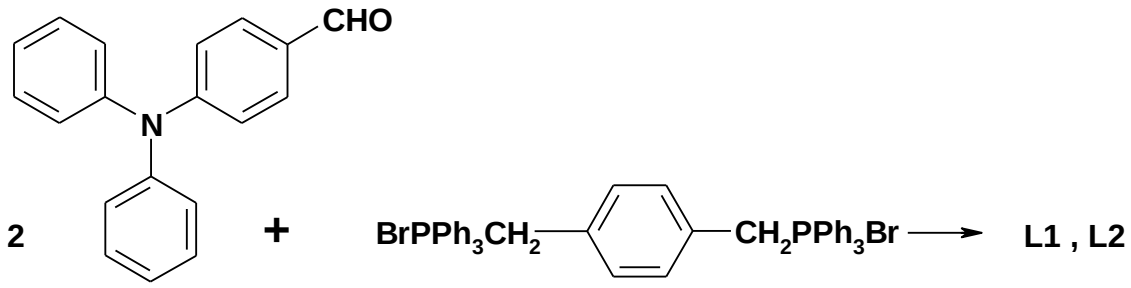
$E_g = E_{HOMO} - E_{LUMO}$

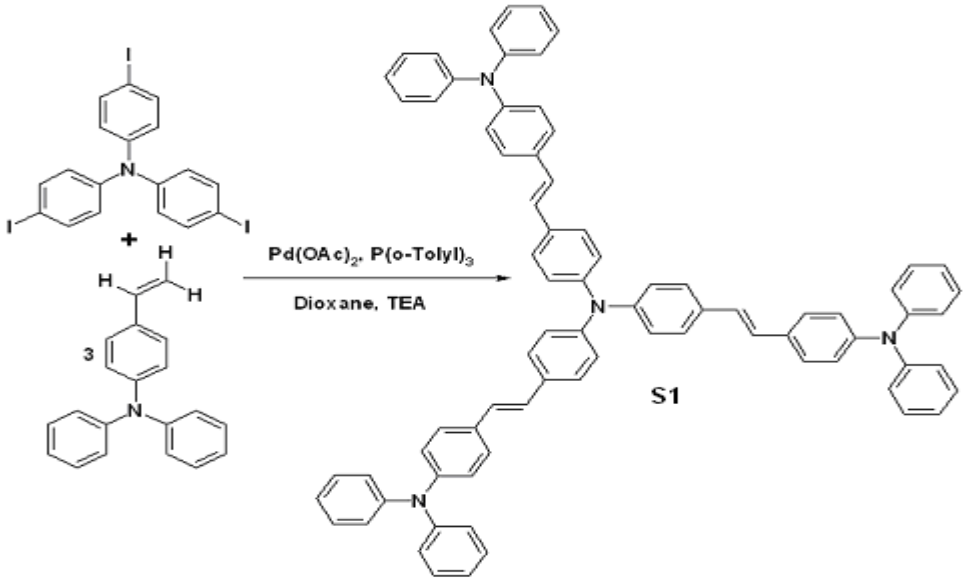
**Linear, star and dendrimer oligomers: synthesis ad characterization**

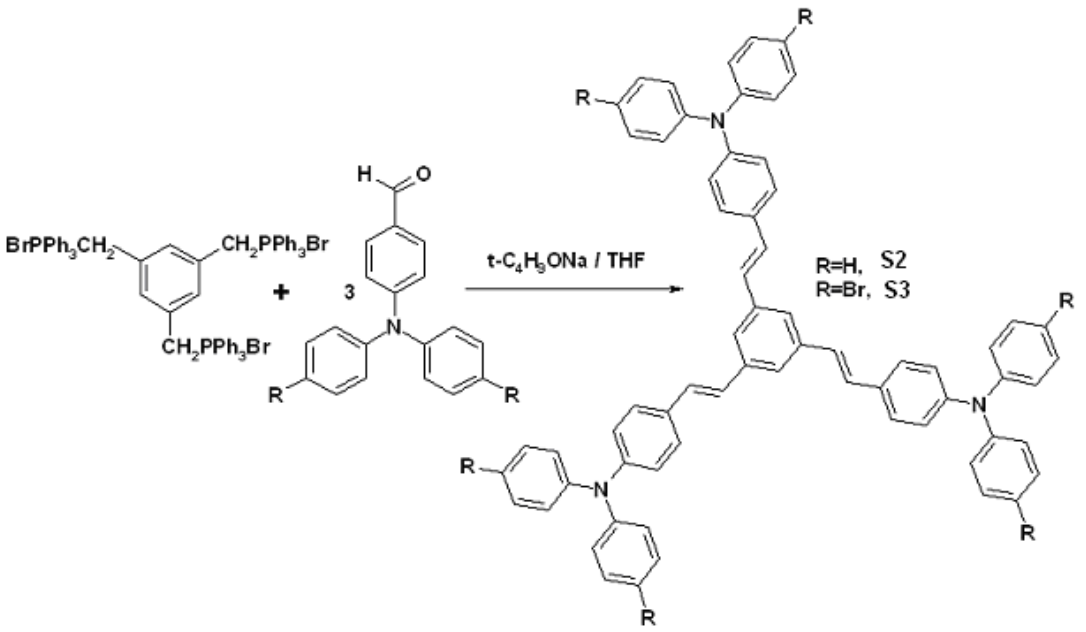
Conjugated oligomers with linear, highly branched and dendrimer structures form an important class of electro- and photoactive materials, investigated both in academic and industrial laboratories. These architectures have advantages to offer molecules with a well-defined form and structure, a high chemical purity and degree of order, being characterized by a polydispersity degree of one. It is important to note that the purity of materials is vital for the long-term stability of optoelectronic devices. Dendrimers can be obtained using laborious step-by-step synthesis in a convergent or divergent methodology. The advantage of using small conjugated compounds is based on the possibility of tuning their photophysical properties by changing the chemical structure, e.g. by introduction of side substituents, end-capping groups, insertion of certain specific functional groups and by changing the oligomer length. Moreover, conjugated oligomers are used as model compounds for conducting polymers since their monodispersity, defectless structure and better supramolecular organization in the solid state facilitate their experimental and theoretical investigations. The real interests for conjugated oligomers emerge also from interesting application such as active components in organic electronic or electrochemical devices, such as organic light emitting diodes (OLEDs), photovoltaic cells, optical power limiting, and field-effect transistors. The structure of oligomers used for these studies is presented in Scheme 3.

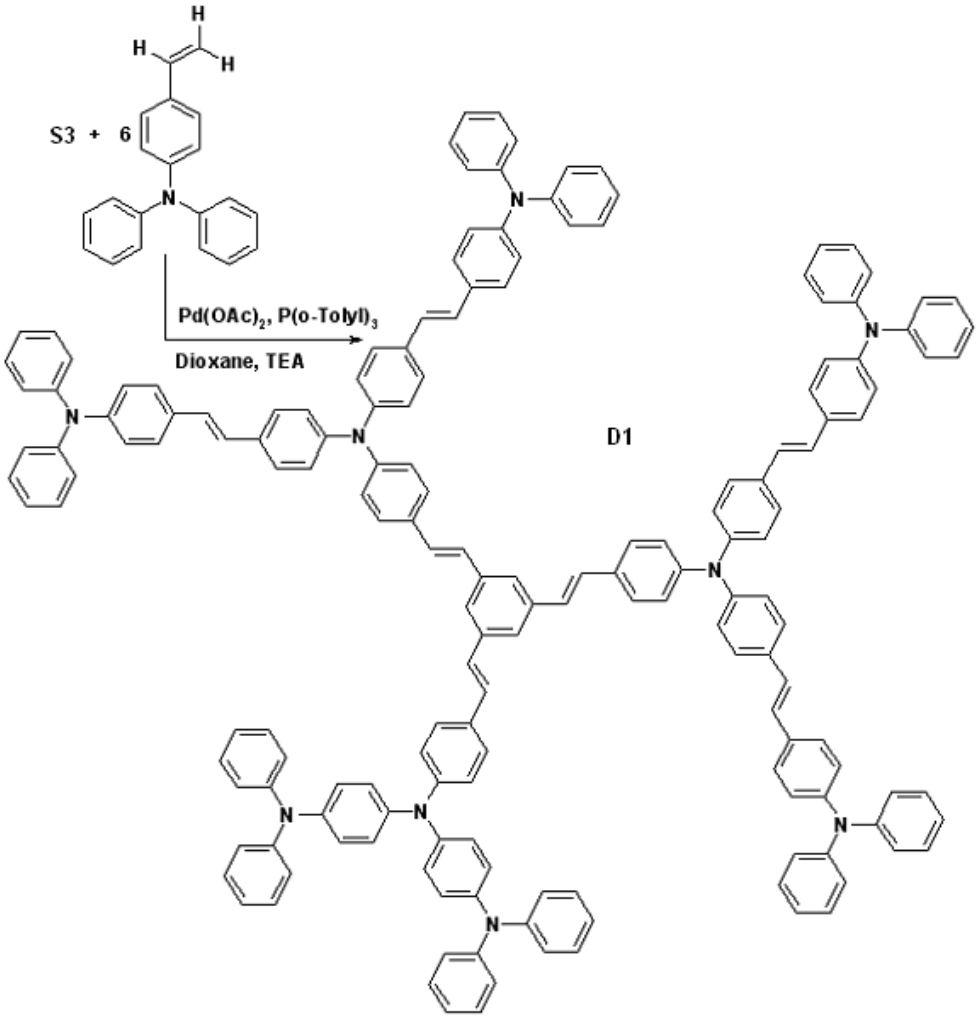



***Scheme 3:*** *Oligomers with linear (L1, l2), starburst (s1, s2) and dendrimer (D1) structure*




BrPPh3CH2
CH2PPh3Br
CH2PPh3Br
+ 3
t-C4H9ONa / THF
R=H, S2
R=Br, S3


S3 + 6
Pd(OAc)2, P(o-Tolyl)3
Dioxane, TEA
D1

***Scheme 4:*** *Synthesis of linear, star-shaped and dendrimer oligomers*

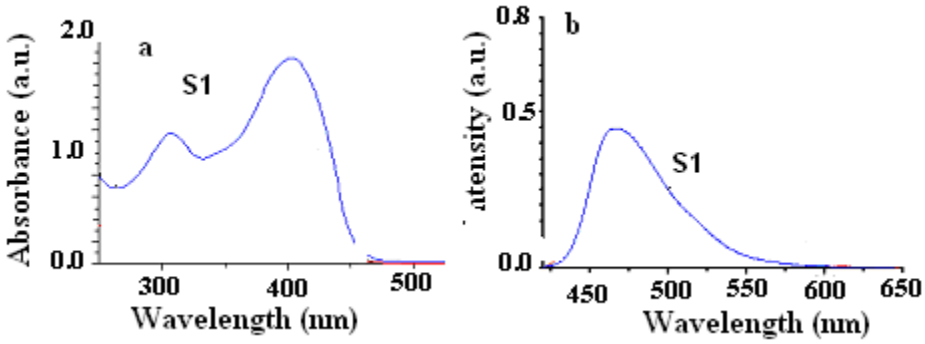



***Figure 3:*** *Absorption (a) and fluorescence (b) spectra of conjugated oligomers with triphenylamine core(S1) in dilute chloroform solution ($10^{-5}$ M). Emission spectra were obtained upon excitation at the absorption maximum.*

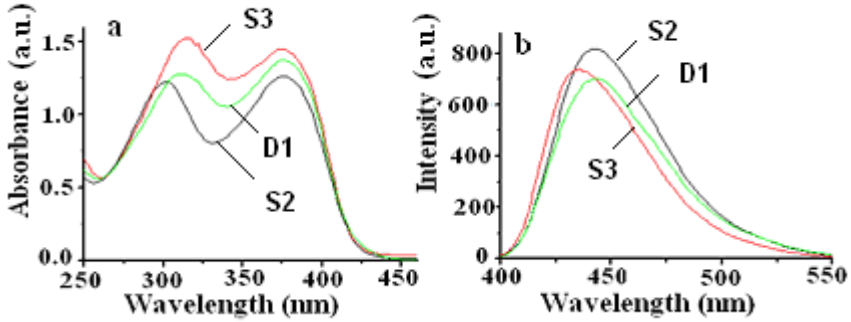



***Figure 4:*** *Absorption (a) and fluorescence (b) spectra of conjugated oligomers with benzene core in dilute chloroform solution ($10^{-5}$ M). Emission spectra were obtained upon excitation at the absorption maximum.*

***Table 2:*** *Optical characteristics of oligomers*

| Oligomer | $\lambda_{abs}^{max}$ (nm)[a)] | $\lambda_{em}^{max}$ (nm)[a)] | $E_g$ (eV)[b)] | Φ |
|---|---|---|---|---|
| L1 | 306;410 | 467;500 | 2.69 | **0.375** |
| L2 | 244;310;392 | 434;461 | 2.79 | **0.707** |
| S1 | 308, 330, 406 | 465 | 2.71 | |
| S2 | 302, 374 | 443 | 2.92 | |
| D1 | 310, 376 | 445 | 2.94 | |

Determinate în soluţii diluate de $CHCl_3$; b) obţinute din spectrul de UV-Vis: Eg = $1240/\lambda_{onset}$

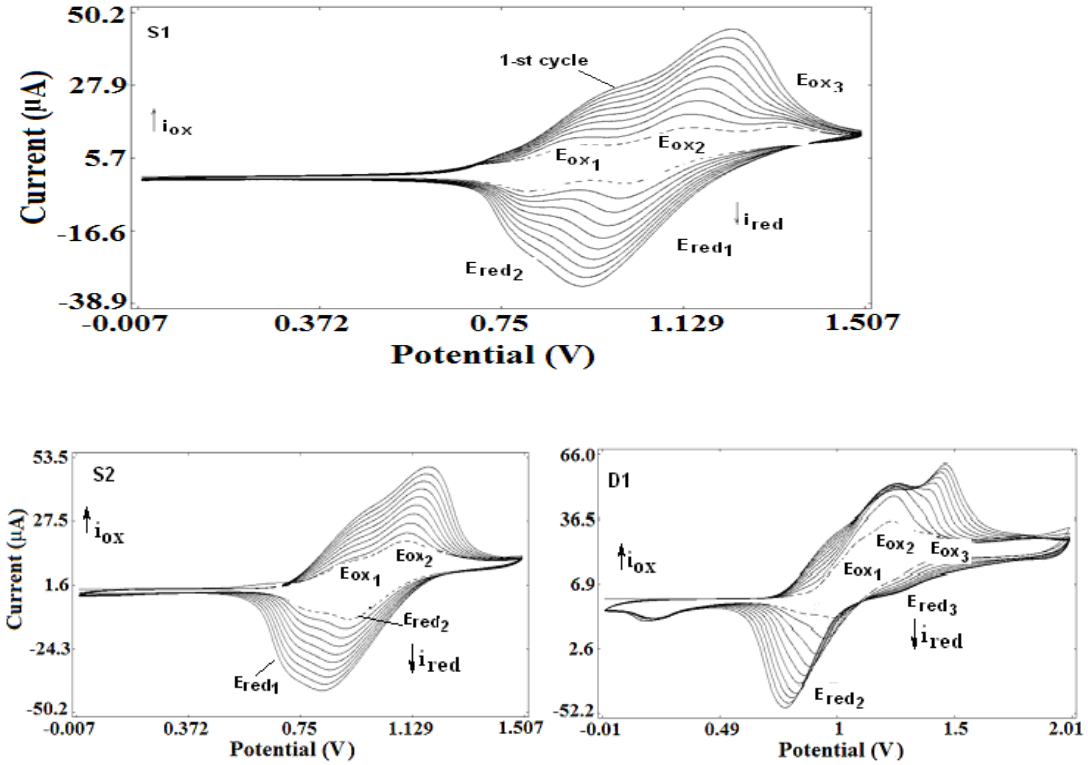


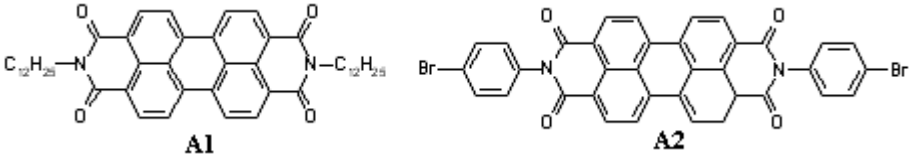

***Figure 5:*** *Cyclic voltammograms for compound S1, S2 and D1, $10^{-3}$ M, using $Bu_4NBF_4$ as support electrolyte ($10^{-1}$M). Scan rate: 50 mV/s between 0.0 and 2.01 V vs Ag/AgCl*

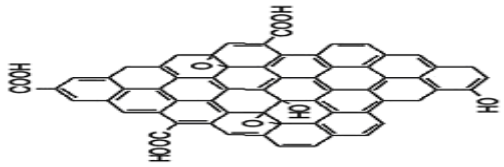
***Table 3:*** *Electrochemical parameters of oligomers*

| Oligomer | $E_{ox}^{onset}$ (V) versus Ag/AgCl | $E_{red}^{onset}$ (V) versus Ag/AgCl | $E_{HOMO}$ (e V) | $E_{LUMO}$ (e V) | $E_g^a$ (e V) |
|---|---|---|---|---|---|
| L1 | 0,791 | - | -5.07 | -2,38 | 2,69 |
| L2 | 0,824 | - | -5,10 | -2,35 | 2,75 |
| S1 | 0,76 | 1,13 | -5,10 | -3,21 | 1,89 |
| S2 | 0,77 | 1,07 | -5,11 | -3,27 | 1,84 |
| D1 | 0,89 | 1,13 | -5,23 | -3,21 | 2,02 |

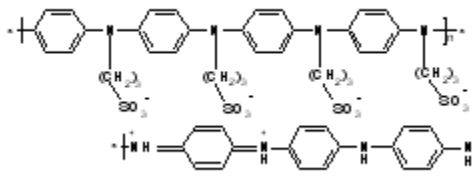
[a]$E_g = E_{HOMO} - E_{LUMO}$

**New acceptor compounds**






GO



PANi/PAN-SO3H