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Synthesis and characterization of new cyanovinyl-substituted branched copolymers having triphenylbenzene as core

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Abstract: New cyano-substituted branched copolymers having 1,3,5-triphenylbenzene (TPB) as core and *p*-phenylenevinylene as connecting groups were synthesized *via* Knoevenagel condensation reaction. For structure studies and due to the poor solubilities of the resulting polymers a model compound has been synthesized. The spectroscopic methods that were used in polymer characterizations are ^{1}H-NMR and FT-IR spectroscopy, UV-Vis and fluorescence spectroscopy. A cyclic voltammetry was performed for model compound, in order to estimate the redox activity of these polymers.

Keywords: Triphenylbenzene; Knoevenagel condensation; Cyanovinylene groups; Cyclic voltammetry.

Introduction

Since 1896, the Knoevenagel condensation had been defined as the reaction between an aldehyde or ketone and any compound having an active

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methylene group.[1] The activation of methylene group is due to the direct attachment of electron withdrawing groups such as nitro, cyano or acyl, and in most cases two such groups are required to provide sufficient activation. The product obtained is an unsaturated compound. There are many papers which describe the synthesis and characteristics of cyano-phenylene-vinylene polymers by Knoevenagel condensation.[2-4] Among other many possibilities to attach various substituents to the polymeric chain, binding the cyano group to an vinylene units is very attractive since it was discovered that the presence of cyano group can increase the photoluminescence (PL) of the polymer. In addition, cyano is a bulky moiety and its inclusion into polymer chain can lead to changes in the properties of the polymer and in particular in the steric hindrance. On the other hand, the introduction of cyano groups on the vinyl position into the polymer main chain can improve the electron affinity of the materials and in addition, these polymers will exhibit a lower energy level of the LUMO.[5-9] As a results, the emission of the compounds is shifted to the longer wavelength region.

One important approach to enhance the PL performance, especially life time of device, is to incorporate vinylene linkage between aromatic rings. The vinylene linkage not only acts as a “conjugation bridge” but also enhances electroluminescence (EL) characteristics and reduces steric interactions between aromatic rings, therefore decreasing the free rotation between units.[10]

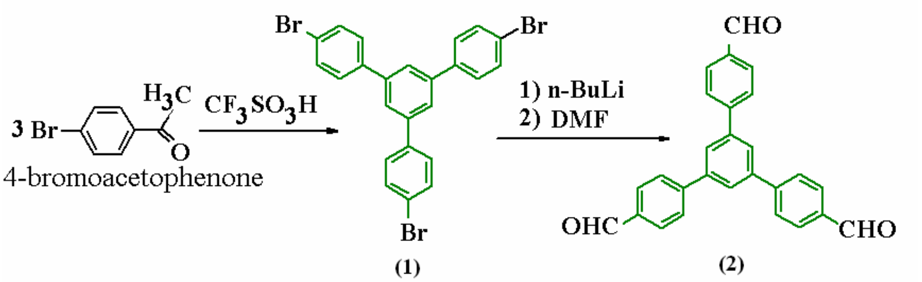
Triphenylbenzene (TPB) is a bulky molecule and is responsible for the propeller-like conformation of the structures. Binding this molecule as a core into the PPV backbone significantly modifies the rod-like molecular conformation of the copolymers by maintaining a large distance between the conjugated branches, thus preventing sterical hindrances.

In the solid state, TPB is like an orthorhombic crystal, and the torsion angle between the phenyl rings is in the range 40-45°.[11] Such a twist torsional angle is responsible for ~ 11 Kcal/mol stabilization compared to the flat conformation for steric reasons.[12] However, one of the phenyl rings was found to be twisted in the opposite direction in order to gain a maximum crystalline packing energy.[13]

The aim of this paper is to investigate the physico-chemical characteristics of a serie of poly(phenylenevinylene) based on TPB units bearing cyano groups attached to the backbone of the polymers. We also describe the synthesis of these branched polymers.

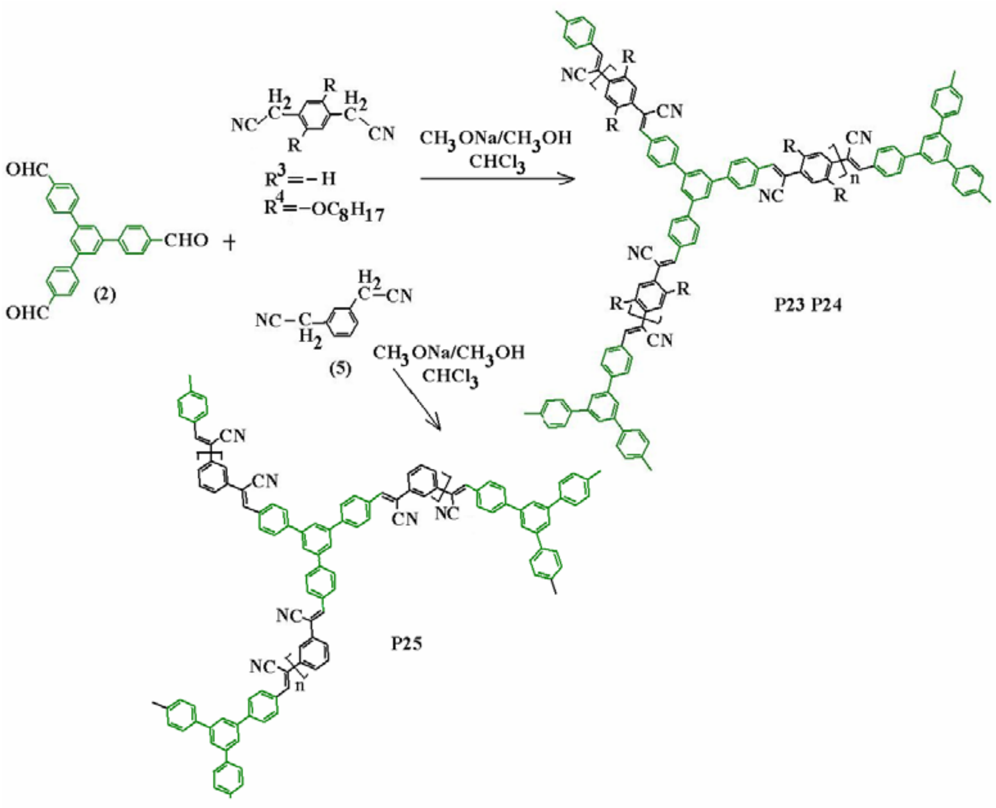
Results and discussions

A three-branch molecule derived from the TPB core adopts a propeller-like conformation where the three phenyl substituents on the central phenyl unit are twisted by about 45°. In order to obtain the suitable monomer to performe the polycondensation reactions, firstly 1,3,5-tri(4-bromophenyl)benzene (1) was synthesized by condensation of three molecules of 4-bromoacetophenone in the presence of catalytic trifluoromethane sulfonic acid (CF_3SO_3H) (Scheme 1).



Scheme 1

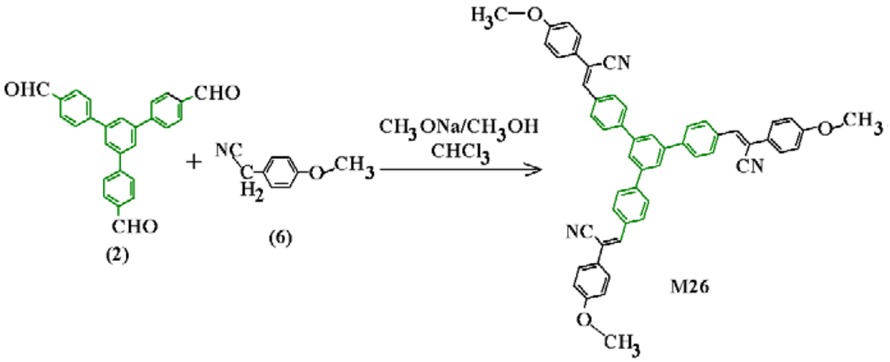
The core reagent (2) was prepared in a three-step procedure based on cyclotrimerization of 4-bromoacetophenone, followed by lithiation and formylation (Scheme 1). The conversion of (1) into (2) was achieved with 56% yield by using the right reaction conditions. The compound appears like light-brown crystals. Having three functional aldehyde groups, this molecules can react via Knoevenagel mechanism with aromatic diacetonitril derivatives resulting hyper-branched structures (Scheme 2).



Scheme 2

The polycondensation reaction was caried out at room temperature for 20-24 h. All reaction characteristics are summarized in Table 1. The resulting polymers were partially soluble in chloroform, with a very low yield of soluble fraction. Incorporation of the alkoxy substituents in polymer did not enhance the solubility of these copolymers as much as we would have anticipated. Larger alkoxy chain, 2,5-alkoxy cyano-substituted polymer (P24) was synthesized, but the yield during the Knoevenagel condensation was very low. This was probably due to increasing steric hindrance of the larger alkoxy chains.

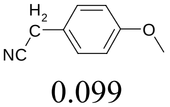
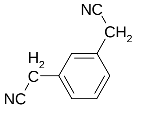
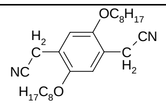
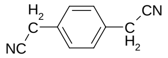
Due to the poor solubilities and in order to confirm the structures of the polymers and to make correlations between the structure and the physico-chemical properties, a model compound (M26) was synthesized *via* the same method and conditions, using (4-methoxyphenyl)acetonitril and 1,3,5-tri(4-formylphenyl)benzene as starting materials (Scheme 3).



Scheme 3

The model compound (M26) was obtained as a light yellow powder with a green fluorescence. It was obtained with 52% yield as soluble fraction in chloroform.

Table 1. The main characteristics of the reactions.

Reaction product	Monomer		Yield (%)		Reaction time (h)	Observations
	$C_{trialdehyde}$ (mol/L)	$C_{cyano\text{-}derivative}$ (mol/L)	$\eta_{soluble}$ %	η_{total} %		
M26	0.033	 0.099	52	52	24	Light-yelow powder
P25	0.035	 0.052	13	78	22	Yelow powder
P24	0.026	 0.04	6	14	24	Light-yelow powder
P23	0.035	 0.052	6	75	20	Orange powder

The ^{1}H NMR spectra of the M26 is in acordance with the proposed structure. The characteristic peak for aldehyde proton, that appeared at 10.10 ppm in the ^{1}H NMR spectra of compound (**2**), is missing indicating that the entire amount of starting material was transformed (Figure 1). The shift of peak corresponding to vinylic protons can be assigned to the presence of electron withdrawing -CN groups. So, the protons of vinylic groups appeared as a singlet at 7.49 ppm. The peaks coresponding protons of phenyl unit appeared in the range 7.64-6.97 ppm, with a slightly shift compared to the ^{1}H NMR spectra for the initial (4-methoxyphenyl) acetonitril. The protons for triphenylbenzene unit can be clearly seen in range of 8.02-7.80 ppm. The assignment of protons is presented in Figure 1.

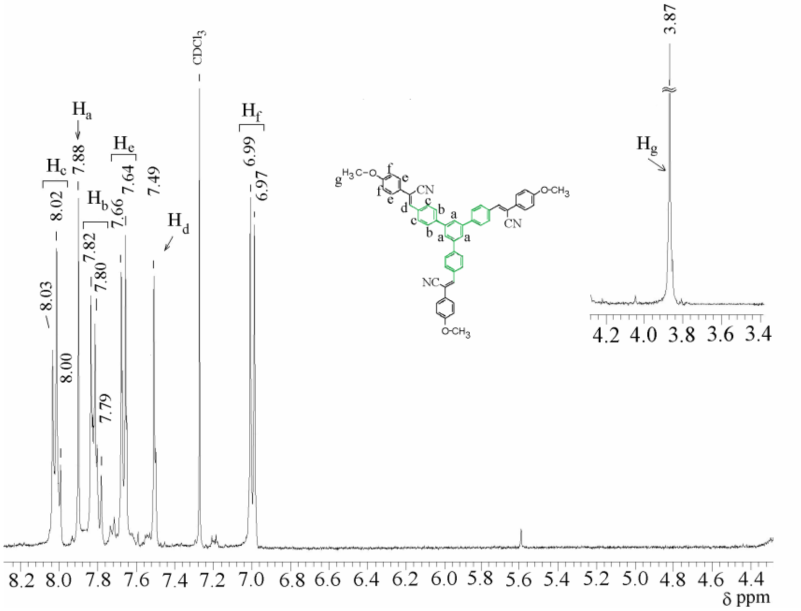


Figure 1. ^{1}H NMR spectra for M26.

In case of polymers, the ^{1}H NMR spectra are broad but the assignment of other signals is in accordance with the structures proposed in Scheme 2 (Figure 2).

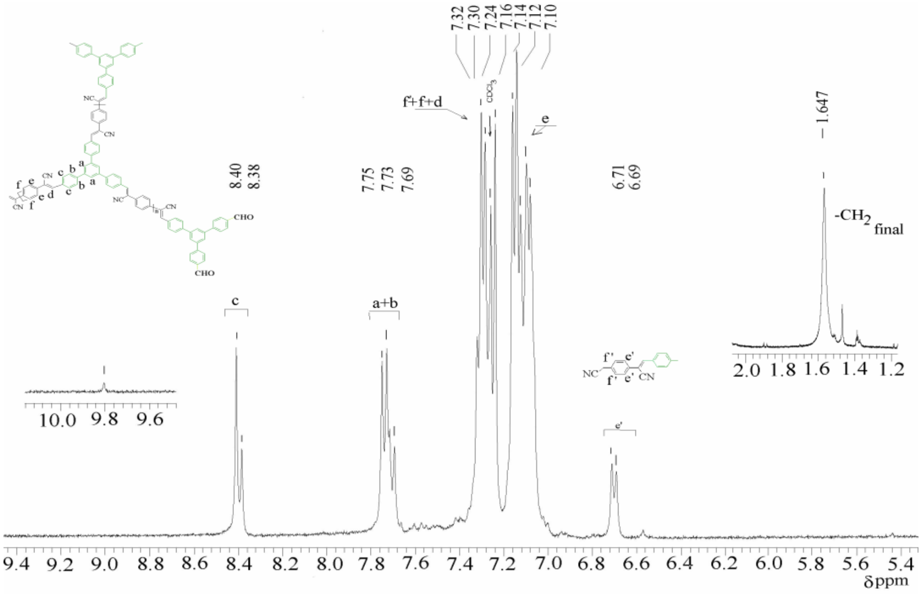


Figure 2. The ^{1}H NMR for P23.

As can be observed in Figure 3 the FT-IR spectrum of M26 do not show any absorption for aldehyde C=O (1680 cm^{-1}) in agreement with ^{1}H NMR spectra for the same compound. Due to the low molecular weight of the polymer, the terminal –CHO (1687 cm^{-1}) groups are observed, mainly in the spectrum of the polymer P23. The presence of the -C≡N groups can be clearly distinguished as a sharp absorption peak in the range (2212 - 2251) cm^{-1}. The –C=C- aromatic absorption bands appear at 1514 cm^{-1} while 814 and 864 cm^{-1} peaks are assigned to out-of-plane deformation of the C-H bonds in the 1,3,5-trisubstituted benzene.

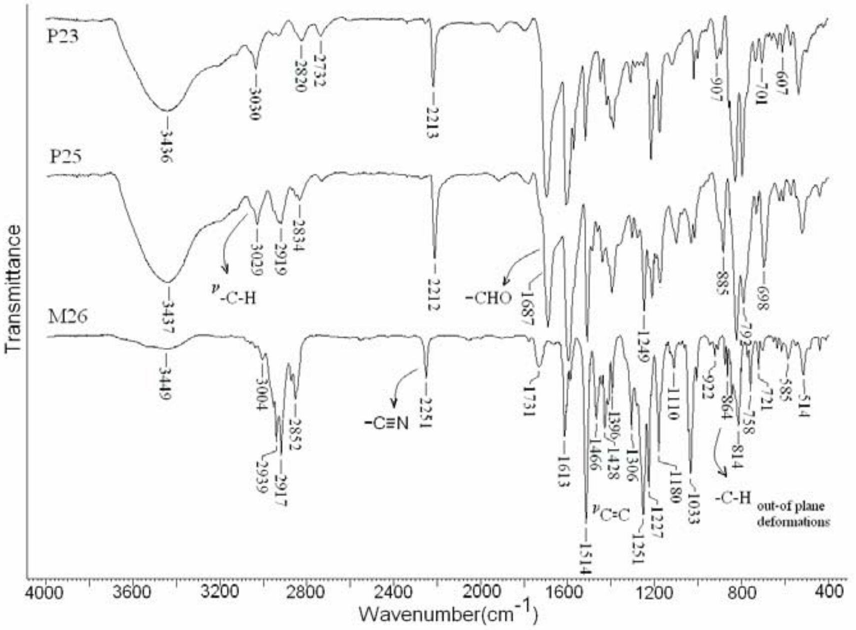


Figure 3. FT-IR spectra for M26 and polymers P23 and P24.

Optical properties:

The optical spectra of model compound and of copolymers P23 and P24 recorded in methylene chloride are presented in Figure 4. As it can be seen in the absorption spectra, the copolymers and model compound exhibit absorption peaks at about 266 nm and 278 nm, characteristic of π -π* transition in aromatic rings. The peaks that appeared in range of (350-360) nm can be attributed to the conjugation of vinyl double bonds with aromatic rings. A net bathochromic shift of the absorption band and a hypochromic effect of absorbance is observed for the model compound (M26) as compared to copolymers. This shift may be assigned to the presence of the electrono-donor (methoxy) and acceptor (nitril) groups, and formation of a intramolecular charge transfer complex. It can be seen that in both absorption and emission spectra, sholders appeared for each polymers located at 283 nm (absorption) and 475 nm (emision) for P23, and at 306 nm (absorption) and 438 (emission) for P24. This may be due to the high structural polydispersity of these polymers but also to the formation of intramolecular charge transfer complex.

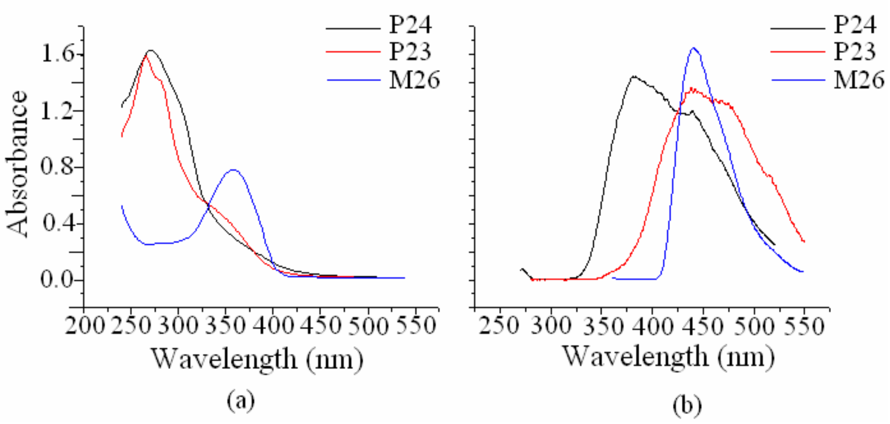


Figure 4. The absorption (a) and fluorescence (b) spectra for model compound (M26) (λ_{exc}=358 nm), and polymers P23 (λ_{exc}=266 nm) and P24 (λ_{exc}=272 nm).

Upon UV excitation, the solutions showed intense fluorescence with maxima at 438 nm. However, the emission spectra are broader for polymers due to their structural polydispersity. The optical data are sumarized in

Table 2. From the onset of the wavelength of absorption peaks can be estimated the values of the optical band gap energy (E_g^{opt}.= λ_{onset} /1240).

Table 2. Optical data of M26 and copolymers P23 and P24.

Comp.	$^{a)}\lambda_{abs}$ (nm)	$^{a),}\lambda_{abs}^{onset}$ (nm)	$^{a)}\lambda_{em}$ (nm)	$E_g^{opt.}$ (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
M26	283; 358	407	442; 475	0.33	-5.80	-3.26
P23	266;283;345	331	438	0.26	--	--
P24	272;306	347	370;438	0.28	--	--

a) measured in diluted CH_2Cl_2 solution;

Electrochemical properties

Electrochemical cyclic voltammetry is often performed for determining the HOMO and LUMO energy levels of conjugated polymers.[14]

The oxidation process corresponds to the removal of charge from the highest occupied molecular orbital (HOMO) band, whereas the reduction cycle corresponds to the filling of the energy state by electrons to the lowest unoccupied molecular orbital (LUMO) band. Therefore, the onset oxidation and reduction potentials were closely related to the energies of the HOMO and LUMO levels of an organic molecule and thus can provide important informations regarding the magnitude of the energy gap. Because of the exact structure of the model compound, we selected it to be analized by cyclic voltammetry. A typically cyclic voltammogram, recorded in the positive range of potentials, for the model compound is presented in Figure 5.

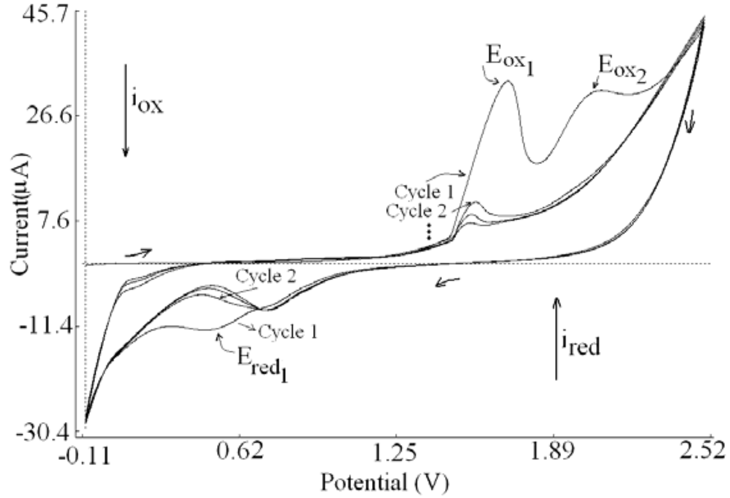


Figure 5. Cyclic Voltammogram of M26, $2X10^{-3}M$, Bu_4NBF_4 was used as support electrolyte, $2X10^{-1}M$. Scan rate: 50 mV/s, 4 cycles.

It can be seen that the compound (M26) reveals in the anodic range of potentials, two irreversible oxidation peaks, at E_{ox1} = 1.710V (I_{ox1}= 32.83 μA), and E_{ox2} = 2.065 V (I_{ox2}= 31.13 μA). In the reverse scanning, M26 reveals only one irreversible reduction peak at E_{red} = 0.504 V (I_{red}= -12.19 μA). Increasing the number of scans, the second peak at 2.065 V disappeared and this may be because of the instability of the compound. The first peak is shifted to more negative values of potentials and this value maintaines constantly with increasing the number of scans. The reduction peak is shifted to more positive potential after second scan and the value of the new peak is 0.737 V. It can be observed that both peaks, oxidation and reduction peaks, appear constantly at the same value of potentials and it seems like the system reaches at an equilibrium state.

The HOMO energy levels can be calculated from CV using first oxidation peak. Assuming that the HOMO energy level for the ferrocene/ferrocenium ion standard is 4.46 eV with respect to the zero vacuum level we can calculated the energy levels for HOMO and LUMO considering the below equations:[15]

$$E_{HOMO} = - e\ (E_{ox}^{onset} + 4.34);$$

$$E_{LUMO} = - e\ (E_{red}^{onset} + 4.34).$$

The value of E_{HOMO} energy level is -5.80 eV and the value of E_{LUMO} energy level is -3.26 eV.

Experimental

Materials

Cyano-derivatives are commercial products (Aldrich Chemical Co.) and were used as received; 4-bromoacetophenone was synthesized according to the literature.[16] All solvents achieved from commercial source and used in this study were purified according to standard methods. Sodium methoxide (CH_3ONa) was obtained by adding sodium metal (0.6 g) in 10 mL dry methanol, under N_2. Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was synthesized by a neutralization reaction of tetrabutylammonium hydroxide solution (40%) with fluoroboric acid (40% solution), both from Fluka, and recrystallized twice from ethyl acetate and then dried *in vacuo* prior to use.

Instrumentation

The FT-IR spectra were recorded in KBr pellets on a Digilab-FTS 2000 spectrometer, while UV-*Vis* absorption spectra and fluorescence measurements were carried out in CH_2Cl_2 solution, on a Specord 200 spectrophotometer and Perkin Elmer LS 55 apparatus, respectively. ^1H-NMR spectra were recorded at room temperature on a Bruker Avance DRX-

400 spectrometer (400 MHz) as solutions in $CDCl_3$ and chemical shifts are reported in ppm and referenced to TMS as internal standard.

The electrochemical studies were carried out using Bioanalytical System, Potentiostat–Galvanostat (BAS 100B/W). Electrochemical experiments were carried out in a three-electrode cell consisting of a platinum disk working electrode (1.6 mm diameter), a platinum wire as auxiliary electrode, and a reference electrode consisted of a silver wire coated with silver chloride. Cyclic voltammograms of the investigated compounds were recorded in degassed dichloromethane solution containing tetrabuthylammonium tertafluoroborate (Bu_4NBF_4) as electrolyte. All the measurements were performed at room temperature, under nitrogen atmosphere. For calibration of the reference electrode, was used at the beginning of the experiments ferrocene/ferrocinium couple ($E^{\circ}_{Fc/Fc+}$= 0.46V *vs* the Ag/AgCl reference) as internal standard, by running the CV of an identical cell without any compound in the system.

Synthesis

Synthesis of 1,3,5-tri(4-formylphenyl)benzene (2)

To a stirred solution of 1,3,5-tri(4-bromophenyl)benzene (1) (5g, 9.2 mmol) in anhydrous benzene (150 mL) under nitrogen atmosphere was slowly added n-BuLi (1,6 M in hexane, 50 mL, 80 mmol) and the mixture turned violet. Then the solution was warmed at 60 °C for 4 h. After cooling at 0 °C, the mixture was cannulated into another flask containing N,N’-dimethylformamide (15 mL). After being stirred for another 4 h at room temperature, the yellow solution was hydrolyzed with aqueous HCl (3N, 100 mL) and the organic layer was separated and evaporated. CH_2Cl_2 was added to the resulting orange oil, and this solution was washed twice with water. By recrystallization from acetic acid the desired compound (2) can be obtained as brown crystals in 70% yield.

^{1}H NMR (400 Hz, $CDCl_3$): δ = 10.10 (s, 3H); 8.04-8.02 (d, J = 8 Hz, 6H); 7.91 (s, 3H); 7.88-7.86 (d, J = 8Hz, 6H);

FT-IR (KBr, cm^{-1}): 1695 (υ-CHO); 1600 (C=C); 800 (υ bezene *p*-disubstituted); 700-600 (υ benzene 1,3,5- substituted).

Synthesis of polymers- general procedure

1,3,5-(4-formylphenyl)benzene (2) (0.15 g, 0.3 mmol) and 1,4-phenylene diacetonitril (3) (0.09 g, 0.5 mmol) were added to the mixture solution of anhydrous chloroform (10 mL) and dry ethanol (2 mL). After the addition, sodium ethoxide (4 mL, 2.33 M), was added by droping to the reaction mixture. The reaction solution was stirred for 24 h at room temperature. After the reaction ended, the mixture was poured into a large amount of methanol and then filltred off and dried. Then the polymer was fractioned by precipitation from chloroform in methanol, and a majority of insoluble fraction was obtained, 75% yield. The soluble polymers fraction was obtained like light-yellow powder with 6 % yield.

The synthesis of polymers P24 and P25 followed the same procedure described for P23.

Synthesis of model compound (M26)

To a mixture of anhydrous chloroform (8 mL) and dry ethanol (2 mL) was added 1,3,5-tri(4-formylphenyl)benzene (2) (0.1g, 0.3 mmol) and 4-methoxyphenyl acetonitril (0.14 mL, 0.9 mmol). Using a dropping funnel, was added by droping, sodium ethoxide (4 mL, 2.9M) under nitrogen atmosphere. The reaction solution was stirred at room temperature for 20 h, and then was poured into a large amount of methanol. The precipitate was filtered off and dried. In order to obtained a pure desired compound, the crude compound was purified by column chromatography using a mixture of solvents of methylene chloride and hexane (4.5:0.5/v:v) as eluent. The pure compound was obtained as yellow powder with 52% yield.

^{1}H NMR (400Hz, $CDCl_3$): δ = 8.02-7.99 (d, J = 8.0 Hz, 6 H); 7.88 (s, 3H); 7.82-7.79 (dd, J = 8.4 Hz, 6H); 7.66-7.63 (d, J = 8.8 Hz, 6H); 7.49 (s, 3H, vinylic protons); 6.99-6.97 (d, J = 8.8 Hz, 6H).

FT-IR (KBr, cm^{-1}): 2251 (υ C≡N); 1687-1731 (C-O); 2852-2939 (C-H, CH_3 deformation);

Conclusions

In summary, branched - phenylenevinylene polymers with cyanovinyl substituents at different positions were synthesized via Knoevenagel reaction. Their structures were characterized by spectroscopic methods like ^{1}H NMR, UV-Vis, and FT-IR. In order to determine with precision the structure of the polymers and to make same correlations between the structure and physico-chemical properties a model compound (M26) was synthesized. Cyclic Voltammetry was carried out in order to obtain information about the electrochemical stability and the reversibility of the redox process of M26. The model compound presented redox activity in the range of potential 0-2 V *vs* Ag/AgCl. Knowing this redox and chemical information, the highest occupied (HOMO) and lowest unoccupied (LUMO) energies of chemical systems can be tuned to lead to new and improved hole-transporting materials. From the onset potentials of both oxidation and reduction and using the classical equations, the LUMO and HOMO energy were calculated.

Acknowledgements

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