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# Photophysical properties of isoelectronic oligomers with vinylene, imine, azine and ethynylene spacers bearing triphenylamine and carbazole end-groups

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# 1. Introduction

# Conjugated oligomers are an important class of electro- and photoactive materials, investigated both in academic and industrial laboratories [1–5]. The great interest for conjugated oligomers emerges from their applications such as active components in organic electronic or electrochemical devices [6,7]. 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. Thus, conjugated oligomers are used as model compounds for conducting polymers since their monodisperse, defectless structure and better supramolecular organization in the solid state facilitate their experimental and theoretical investigations [8].

During the last years, much attention has been paid to triphenylamine (TPA) and carbazole compounds due to their electron donating and hole-transporting properties, making these compounds promising candidates for electroluminescent and photorefractive devices [9–12]. Many triphenylamine-based dyes are used in dye-sensitized solar cells as sensitizers [13–15] and numerous

# ABSTRACT

Ten symmetrical oligomers containing either triphenylamine or carbazole substituents as end-groups and 1,4-phenylenevinylene, 1,4-phenylene imine, azine and 1,4-phenylene ethynylene as  $\pi$ -spacers, have been synthesized by polycondensation reactions between aromatic aldehydes (4-formyltriphenylamine and 3-formyl *N*-hexylcarbazole) or iodides (4-iodotriphenylamine and 3-iodo *N*-hexylcarbazole) with bisphosphonate derivative, 1,4-diaminobenzene, hydrazine or 1,4-diethynylbenzene, respectively. These oligomers are models for the corresponding conducting polymers, have a well-defined molecular structure, can be highly purified using common methods and processed as thin films by vacuum evaporation, dip or spin coating. The oligomers preserve all of the properties and potential applications of the corresponding polymers. The structural characterization of these oligomers was performed using usual spectroscopic methods (<sup>1</sup>H-RMN, FT-IR and DSC) and their photophysical properties were analyzed by UV–Vis and fluorescence spectroscopy. Their redox properties were studied by cyclic voltammetry.

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experimental and theoretical studies were carried out to correlate their structure with spectral properties [16-20]. It is well known that the central amine nitrogen atom is responsible for this donor behavior and these arylamine compounds are commonly used, as photoconductors in the Xerox process in laser printers and photocopiers [21–23]. From the structural point of view, the carbazole molecule differs from diphenylamine by its planar structure, since it can be further imagined as bonded diphenylamine in the orthopositions of phenyl rings, which induce the higher thermal stability of carbazole-containing materials. Triphenylamine is a well-known molecule that possesses useful functions such as redox activity, fluorescence, ferromagnetism due to the ready oxidation of the nitrogen center and hole-transporting properties via radical cation species [24]. Owing to the noncoplanarity of the phenyl substituents, TPA derivatives can be viewed as 3D systems and the combination with linear  $\pi$ -conjugated systems could be expected to lead to amorphous molecular materials (molecular glasses) with isotropic optical and charge-transport properties. Our interests in conjugated arylamine oligomers [25-28] are justified by these interesting properties, and in this paper we report the synthesis of ten symmetrical and isoelectronic arylamine oligomers containing either two triphenylamine or carbazole groups separated by different  $\pi$ -spacers and investigate the influence of the spacer on their photophysical properties.





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# 2. Experimental

# 2.1. Materials and instruments

Aldehyde monomers, 4-formyltriphenylamine [28] and 3formyl *N*-hexylcarbazole [26], and iodide derivatives; 4iodotriphenylamine and 3-iodo *N*-hexylcarbazole [29] were synthesized by adaptation of known methods. Other chemicals:  $\alpha$ ,  $\alpha'$ dichloro-p-xylene (95%), 4,4'-bis(chloromethyl)-1,1'-biphenyl (95%), 1,4-diaminobenzene, benzidine, hydrazine hydrate, 1,4diethynylbenzene, solvents and catalysts (all from Aldrich) were obtained from commercial sources and used as received or purified by standard methods.

*Note*: Benzidine has been linked to bladder and pancreatic cancer and since August 2010 benzidine dyes have been included in the environmental Protection Agency's List of Chemicals of Concern.

The FT-IR spectra were recorded in KBr pellets on a DIGILAB-FTS 2000 spectrometer. <sup>1</sup>H NMR spectra were recorded at room temperature on a Bruker Avance DRX-400 spectrometer (400 MHz) as solutions in CDCl<sub>3</sub> and chemical shifts are reported in ppm and referenced to TMS as internal standard. UV-visible and fluorescence measurements were obtained on a Specord M42 Carl Zeiss Jena spectrophotometer using quartz cells (10 mm) and a Perkin Elmer LS 55 apparatus (Perkin Elmer, Norwalk, CT, USA), in solution. Thermal behavior was determined by DSC method with a Mettler DSC-12E apparatus, in nitrogen atmosphere. Elemental analyses were done with a 2400 II Perkin Elmer Elemental Analyzer. The cvclic voltammograms (CV) reported in this article were recorded using a Bioanalytical System, Potentiostat–Galvanostat (BAS 100B/ W). The electrochemical cell was equipped with three electrodes: a working electrode (disk shape Pt electrode,  $\Phi = 1.6$  mm), an auxiliary electrode (platinum wire), and a reference electrode (consisted of a silver wire coated with AgCl). Before experiments, Pt electrode was polished between each set of experiments with aluminium oxide powder on a polishing cloth, and then was sonicated in a mixture of detergent and methanol for 5 min and then rinsed with a large amount of doubly distilled water. The reference electrode (Ag/Ag+) was calibrated at the beginning of the experiments by running the CV of ferrocene as the internal standard in an identical cell without any compound in the system ( $E_{1/2} = 0.52$  V versus the Ag/AgCl). Prior to the each experiment, the Bu<sub>4</sub>NBF<sub>4</sub> solutions were deoxygenated by passing dry argon gas for 10 min. All measurements were performed at room temperature (25 °C) under argon atmosphere.

# 2.2. Synthesis of arylenevinylene oligomers. General procedure

In a 50 mL two-neck round bottom flask, equipped with a magnetic stirrer, nitrogen inlet-outlet and dropping funnel, aldehyde (0.5 mmol) and chloroform (15 mL) were introduced. At the resulted solution diphosphonium salt (0.25 mmol), dissolved in ethanol (15 mL) was added. A solution of 0.5 M sodium ethoxide (4 mL), freshly prepared, was added in excess to the mixture by dropping. The reaction mixture was stirred at room temperature under nitrogen atmosphere for 12 h. The precipitate was filtered and washed with ethanol. After several purifications by precipitation in methanol from toluene solution, oligomers were obtained as bright colored powders with strong fluorescence in high dilute solution.

**T1:** 1,4-bis [4-(N,N'-diphenylamino)phenylvinyl] benzene was obtained as a yellow crystalline powder with 94% yield. M.p. = 196 °C; FT-IR (KBr)  $\nu$ , cm<sup>-1</sup>: 3023–2920 (=C-H), 1598, 1492 (C-C monosubstituted phenyl), 1589 (C=C, conjugated phenyl group), 1328 (C–N stretching vibration), 960 (out-of-plane bending vibration of HC=CH *trans*), 827 (CH *p*-substituted benzene ring), 697–695 (C–H phenyl rings). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ , ppm: 7.47 (s, 4H), 7.40–7.38 (d, 4H, H vinyl, *J* = 8.4 Hz), 7.28–7.24 (t, 8H, *J* = 8.4 Hz), 7.12–7.09 (d, 8H, *J* = 7.6 Hz), 7.06–6.96 (m, 12H). Anal. found: C, 89.40; H, 5.80; N, 4.65. C<sub>46</sub>H<sub>36</sub>N<sub>2</sub> (616.808) requires C, 89.57; H, 5.88; N, 4.55.

**K1**: 3,3'-bis (*N*-hexylcarbazolyl)vinylbenzene was synthesized as a yellow crystalline powder with 95% yield. M.p. = 170 °C. FT-IR (KBr) ν, cm<sup>-1</sup>: 3435 (=C–H), 2956, 2856 (N–C), 1598, 1491, 1477 (C–C monosubstituted benzene) 1351 (=C–N), 1154 (–C–N stretching vibration), 962 (out-of-plane bending vibration of HC=CH *trans*), 814 (CH *p*-substituted benzene ring). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ, ppm: 8.26 (s, 2H), 8.16 (d, 2H, *J* = 7.6 Hz), 7.69 (dd, 2H, *J* = 8.4 Hz, *J* = 1.2 Hz), 7.50 (s, 2H), 7.42–7.23 (m, 6H), 7.36 and 7.18 (4H, H vinyl *trans*, *J* = 16.4 Hz), 7.58 (4H, H<sub>phenyl</sub>), 4.28 (4H, –N–CH<sub>2</sub>), 1.88 (4H, –CH<sub>2</sub>–), 1.31–1.43 (12H, –(CH<sub>2</sub>)<sub>3</sub>), 0.89 (6H, t, – CH<sub>3</sub>). Anal. found: C, 87.42; H, 7.60; N, 4.55. C<sub>46</sub>H<sub>48</sub>N<sub>2</sub> (628.904) requires C, 87.84; H, 7.69; N, 4.47.

**T2**: 4,4'-bis [4-(*N*,*N*'-diphenylamino)phenylvinyl]biphenyl was obtained as yellow compound with 79% yield. M.p. = 209 °C. FT-IR (KBr)  $\nu$ , cm<sup>-1</sup>: 3028–3020 (=C–H), 1591 (C–C monosubstituted phenyl), 1586 (C=C, conjugated phenyl group), 1316 (–C–N stretching vibration), 962 (out-of-plane bending vibration of HC=CH trans), 821 (CH *p*-substituted benzene), 697–695 (C–H benzene). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ , ppm: 7.56–7.84 (dd, 8H, *J* = 8.4 Hz, *J* = 1.2 Hz), 7.41–7.39 (d, 4H, *J* = 8.8 Hz), 7.28–7.24 (d, 8H, *J* = 8.0 hz), 7.12–7.10 (d, 8H, *J* = 8.0 Hz), 7.08–7.00 (m, 12H). Anal. found: C, 90.20; H, 5.70; N, 4.15. C<sub>52</sub>H<sub>40</sub>N<sub>2</sub> (692.906) requires C, 90.13; H, 5.82; N, 4.05.

# 2.3. Synthesis of aryleneimine oligomers: general procedure

In a 50 mL two-neck round bottom flask, equipped with a magnetic stirrer and nitrogen inlet-outlet, aldehyde (1 mmol), 1,4-phenylenediamine or benzidine (0.5 mmol) and absolute ethanol (15 mL) were introduced and stirred at room temperature. The solution turned on colored and a crystalline precipitate separated. After several hours the crystalline precipitate was filtered, washed with fresh solvent and purified.

**T3**: *N*,*N'*-*bis*[4-(*diphenylamino*)*benzylidene*]1,4-*phenylenediamine*. Reaction was performed in ethanol, in absence of any catalyst by stirring and heating at 50 °C for 5 h. The product was precipitate in water, filtered, dried and purified by repeated precipitations in water from ethanol solution. Yellow-orange powder. Yield = 92.3%; M.p. = 176 °C. FT-IR (KBr) *v*, cm<sup>-1</sup>: 3410–3015 (=C–H), 2924, 2853 (N–C), 2730, 1615 (–CH=N), 1587 (C=C, conjugated phenyl group), 1506 (C–C monosubstituted phenyl), 1487 (C–C monosubstituted benzene), 1420, 1317 (–C–N stretching vibration), 1268, 1193, 1164, 970 (out-of-plane bending vibration of CH=N), 876 (CH *p*-substituted benzene), 752–615 (C–H phenyl rings). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ, ppm: 8.42 (s, 2H, –CH=N–), 7.76 (d, 4H, phenyl, *J* = 8.8 Hz), 7.08–7.35 (m, 28H, from triphenylamine group). Anal. found: C, 85.20; H, 5.61; N, 9.21. C<sub>44</sub>H<sub>34</sub>N<sub>4</sub> requires (618.784) C, 85.40; H, 5.54; N, 9.06.

**K3**: *N*,*N'*-*bis*(9-*hexyl* 3-*carbazolylmethylidene*)1,4-*phenylenediamine* was obtained yellow-reddish crystals with 55% yield. M.p. = 130–134 °C; FT-IR (KBr) ν, cm<sup>-1</sup>: 3430–3025 (=C–H), 2948, 2854 (N–C), 2170, 1686, 1611 (–CH=N), 1595(C–C monosubstituted phenyl), 1477 (C–C monosubstituted benzene), 1415, 1382, 1323(–C–N stretching vibration), 1262, 1121, 1019, 888, 846, 830 (CH *p*-substituted benzene ring), 744–613 (C–H phenyl rings). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ, ppm: 8.70 (s, 2H, –CH=N–); 8.64 (s, 2H); 8.17 (d, 2H, *J* = 8.6 Hz); 8.06 (d, 2H, *J* = 8.6 Hz); 7.423–7.52 (m, 6H); 7.36 (s, 4H, phenyl); 7.28–7.30 (m, 2H); 4.22 (t, 4H, –N–CH<sub>2</sub>–); 1.77 (t, 4H; –N–C–CH<sub>2</sub>–); 1.17–1.31 (m, 12H, –(CH<sub>2</sub>)<sub>3</sub>–); 0.76 ppm (t, 6H, -CH<sub>3</sub>). Anal. found: C, 83.52; H, 7.43; N, 8.98. C<sub>44</sub>H<sub>46</sub>N<sub>4</sub> (630.88) requires C, 83.76; H, 7.35; N, 8.89.

**T4:** *N,N'-bis*[4-(*diphenylamino*)*benzylidene*]4,4'*diaminobiphenyl* was obtained as pale-yellow solid with 80% yield. M.p. = 245 °C. FT-IR (KBr) ν, cm<sup>-1</sup>: 3430–3025 (=C–H), 2923, 2852 (N–C), 2170, 1692, 1585 (C=C, conjugated phenyl group), 1486, 1422, 1315, 1282, 1164, 1027, 883, 818 (CH *p*-substituted benzene ring), 753, 695 (C–H phenyl rings). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ, ppm: 8.43 (s, 2H, – CH=N–), 7.76 and 7.66 (d, 8H, from biphenyl, *J* = 8.4 Hz), 7.08–7.35 (m, 28H, from triphenylamine group). Anal. found: C, 86.20; H, 5.61; N, 8.23. C<sub>50</sub>H<sub>38</sub>N<sub>4</sub> (694.882) requires C, 86.43; H, 5.51; N, 8.06.

# 2.4. Synthesis of azine oligomers: general procedure

In a 50 mL two-neck round bottom flask, equipped with a magnetic stirrer and nitrogen inlet—outlet, aldehyde (1 mmol) and hydrazine hydrate 100% (0.5 mmol) were dissolved in absolute ethanol (10 mL) and stirred at room temperature. After several hours a crystalline precipitate separated. This crystalline compound was filtrated, washed with fresh solvent and purified by recrystal-lization from ethanol.

**T5**: *N*,*N'*-*bis*[4-(*diphenylamino*)*benzylidene*]*azine* was obtained as bright yellow crystals with 87% yield = 87%. M.p. = 223 °C. FT-IR (KBr) ν, cm<sup>-1</sup>: 3445 (=C–H), 3034, 2923, 2850 (N–C), 1939, 1616, 1590 (C–C monosubstituted phenyl), 1489, 1425, 1331 (–C–N stretching vibration), 1284, 1171, 1075, 966, 899, 832, 752, 697 (out-of-plane bending vibration of –HC=N). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ, ppm: 8.57 (s, 2H, –CH=N–), 7.66 (d, 4H, *J* = 8.4 Hz), 7.31–7.04 (m, 24H). Anal. found: C, 84.33; H, 5.32; N, 10.23. C<sub>38</sub>H<sub>30</sub>N<sub>4</sub> (542.686) requires C, 84.10; H, 5.57; N, 10.33.

**K5**: *N*,*N'*-*bis*(9-*hexyl* 3-*carbazolylmethylidene*)azine. Recrystallized from CHCl<sub>3</sub> as yellow crystalline needles with 84.5% yield; m.p. = 146–147 °C. FT-IR (KBr) *ν*, cm<sup>-1</sup>: 3051 (=C–H), 2948, 2928, 2855 (N–C), 1616, 1596 (C–C monosubstituted phenyl), 1575 (C=C, conjugated phenyl group), 1332 (–C–N stretching vibration), 1217, 1184, 969 (out-of-plane bending vibration of –HC=N), 891, 810 (CH *p*-substituted benzene ring), 744, 730–608 (C–H phenyl rings). <sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz)  $\delta$ , ppm: 8.94 (s, 2H, –CH=N–); 8.58 (s, 2H); 8.17 (d, 2H, *J* = 8.0 Hz); 8.02 (d, 2H, *J* = 8.0 Hz); 7.52–7.42 (m, 6H); 7.30 (t, 2H); 4.32 (t, 4H, –N–CH<sub>2</sub>–); 1.89 (4H, quintet, –N–C–CH<sub>2</sub>–); 1.42–1.26 (m, 12H, –(CH<sub>2</sub>)<sub>3</sub>–) and 0.87 (t, 6H, –CH<sub>3</sub>). Anal. found: C, 82.11; H, 7.54; N, 10.26. C<sub>38</sub>H<sub>42</sub>N<sub>4</sub> (554.782) requires C, 87.84; H, 7.69; N, 4.47.

# 2.5. Synthesis of ethynylene oligomers by Sonogashira coupling: general procedure

In a 50 mL two-neck round bottom flask, equipped with a magnetic stirrer and nitrogen inlet-outlet, iodine derivative

(1 mmol), 1,4-diethynylbenzene (0.5 mmol),  $PdCl_2(PPh_3)_2$ (0.005 mmol), Cul (0.03 mmol), PPh<sub>3</sub> (0.02 mmol) and triethylamine (10 mL) were introduced and stirred at 60 °C for 12 h. Then the reaction mixture was cooled, triethylamine removed at vacuum and solid product washed with water and diluted HCl solution. The product was purified by flash chromatography on silicagel using CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:5) as eluent.

**T6**: 1,4-*Bis*(4-(*diphenylamino*)*phenylethynylene*)*benzene* was obtained as a yellow solid with 85.7% yield. M.p. = 129-130 °C. FT-IR (KBr) ν, cm<sup>-1</sup>: 3435 (=C-H), 3034, 2923, 2852, 2207 (C-C triple bond), 1588, 1513, 1490, 1278, 833. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ, ppm: 7.46 (s, 8H), 7.39–7.35 (t, 4H), 7.29–7.25 (m, 12H), 7.12–7.10 (d, 8H). Anal. found: C, 90.02; H, 5.11; N, 4.67. C<sub>46</sub>H<sub>32</sub>N<sub>2</sub> (618.776) requires C, 90.16; H, 5.26; N, 4.58.

**K6**: 1,4-*Bis*(*N*-*hexyl* 3-*carbazolylethynylene*)benzene was obtained as pale-yellow solid. Yield = 92.9%. M.p. = 79–80 °C, MS-ESI = 625.88 (M + H<sup>+</sup>). FT-IR (KBr)  $\nu$ , cm<sup>-1</sup>: 3449, 3047, 2964, 2926, 2205 (CC triple bond), 1622, 1587, 1474, 1443, 1344, 1271, 1231, 1124, 1082, 885, 789, 743, 719. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$ , ppm: 8.64 (s, 2H), 8.22 (d, 2H, *J* = 8.0 Hz) 7.73 (d, 2H, *J* = 8.4 Hz), 7.64 (d, 2H, *J* = 8.4 Hz), 7.49–7.52 (m, 4H), 7.22–7.25 (t, 2H), 4.27 (q, 4H, –N–CH<sub>2</sub>), 1.76 (m, 4H, –N–C–CH<sub>2</sub>) 1.20–2.27 (m, –(CH<sub>2</sub>)<sub>3</sub>–12H), 0.9 (t, 6H, –CH<sub>3</sub>). Anal. found: C, 88.28; H, 7.18; N, 4.61. C<sub>46</sub>H<sub>44</sub>N<sub>2</sub> (624.872) requires C, 88.41; H, 7.10; N, 4.49.

# 3. Results and discussion

Ten symmetrical oligomers with arylenevinylene, aryleneimine, aryleneazine and aryleneethynylene structures and ether two groups at the termini have been synthesized by polycondensation of aldehydes with bisphosphonate derivatives, diamines or hydrazine, or iodide derivatives with 1,4-diethynylbenzene (Sonogashira coupling), respectively. The synthetic pathways are presented in Scheme 1 and the chemical structures of the compounds are given in Scheme 2.

The aldehydes, 4-(diphenylamino)benzaldehyde and 3-formyl *N*-hexylcarbazole have been synthesized in good yields by a Vilsmeier formylation reaction of the triphenylamine or *N*-hexylcarbazole, respectively. The monoaldehydes were separated as pure compounds by flash chromatography using silicagel and ethylacetate/hexane (1:10) as eluent. Arylenevinylene compounds **T1**, **T2** and **K1** were obtained *via* Wittig condensation of the bisphosphonium salts with the corresponding aldehydes using sodium ethoxyde as base. Imine (**T3**, **T4** and **K3**) and azine (**T5** and **K5**) compounds were obtained by condensation of 1,4-phenylenediamine, benzidine and hydrazine hydrate, respectively, with the requested aldehydes. Ethynylene compounds (**T6** and **K6**) were synthesized by Sonogashira coupling of 1,4-diethynylbenzene with 4-iodotriphenylamine or 3-iodo *N*-hexylcarbazole. The



Scheme 1. Synthesis of arylenevinylene, aryleneimine, aryleneazine and aryleneethynylene oligomers.



Scheme 2. Chemical structures of arylenevinylene, aryleneimine, aryleneazine and aryleneethynylene oligomers.

structures of all compounds were proved by FT-IR, <sup>1</sup>H NMR and elemental analyses.

# 3.1. Absorption properties

All oligomers exhibit absorption bands in the wavelength range from 250 to 550 nm assigned to electronic transitions in the triphenylamine and carbazole chromophores, while almost no linear absorption was observed beyond 550 nm. Fig. 1A presents the absorption spectra of the vinylene oligomers in dilute chloroform solutions with absorption maxima located at around 392 nm (**K1**), 400 nm (**T2**) and 410 nm (**T1**), respectively. Absorption bands located at around 300 nm can be assigned to the electronic  $\pi$ - $\pi$ \* transitions from the aromatic rings, while the absorption maxima located in the range of 390–410 nm can be assigned to electronic  $\pi$ - $\pi$ \* transitions of the conjugated backbone. A clear hypsochromic shift of the absorption maxima of oligomer **T2** (400 nm) with respect to **T1** (410 nm) is observed in the UV spectra, as well as in photoluminescence spectra.

The absorption spectra of aryleneimine oligomers (**T3**, **T4** and **K3**) exhibit bands in the range of 300 nm and 450 nm. In general, by adding the biphenyl segment as a longer  $\pi$ -spacer between the triphenylamine units it should to increase the electronic conjugation pathway in **T2** and **T4** with respect to **T1** and **T3**. However, analyzing the absorption spectra of **T4** with respect to **T3** and **T2** with respect to **T1** it can be observed the exception from this rule. The absorption bands of **T4** and **T2** are blue shifted to lower values with respect to **T3** or **T1**. This behavior could be explained by the fact the two phenyl rings from the biphenyl spacer are twisted one to another with a dihedral angle due to steric hindrance between the *ortho*-hydrogen atoms. This non-coplanarity of the central

biphenyl unit may lead to a diminishing of the  $\pi$ -conjugation of the whole system and a hypsochromic shift of the absorption bands.

UV–vis absorption spectra of azine oligomers **T5** and **K5**, present absorption bands located in the range of 250–325 nm and 350–450 nm. With respect to azine-based carbazole oligomers (**K5**), the triphenylamine-azine oligomer (**T5**) exhibited red-shifted absorption maximum at 410 nm, and this behavior can be explained by an increase of conjugation due to stronger triphenylamine donor units. The same order was observed for ethynylene oligomers, **T6** > **K6**. The absorption data of all oligomers are summarized in Table 1. The energy gaps ( $E_g^{opt}$ ) were determined from the edges of the absorption spectra.

# 3.2. Photoluminescence properties

The photoluminescence spectra were recorded in chloroform solution exciting the samples at maximum absorption peak (Fig. 2).

The blue shifting of absorption maxima of **T2** with respect to **T1**, observed in the UV–Vis absorption spectra, can also be distinguished in PL spectra and this may be explained by decreasing of conjugation length due to nonplanarity of the biphenyl unit. From the point of view of light emitting materials applications, the non-coplanarity of **T2** could be considered an advantage because the electroluminescent materials has to be thermally stable, to present a low tendency for aggregation and excimer formation, crystallization and destruction. The non-coplanar structure of the **T2** inhibits the crystallization and aggregation phenomena (observed by DSC studies). The carbazole-based arylenevinylene oligomers exhibit a blue-yellow fluorescence while the triphenylamine compounds have a green-yellow fluorescence in chlorinated solvents.



**Fig. 1.** UV spectra of arylamine oligomers, recorded in chloroform solution: (A) absorption spectra of arylenevinylene oligomers; (B) absorption spectra of aryleneimine oligomers; (C) absorption spectra of aryleneazine oligomers; and (D) absorption spectra of ethynylene oligomers.

The fluorescence quantum yield was determinated for arylenevinylene oligomers in chloroform solution using 9,10- diphenylanthracene as reference standard ( $\Phi = 0.90$ ) [30]. The fluorescence quantum yield values for **T1**, **K1** and **T2**, are summarized in Table 1, and are in the range of 0.375 and 0.707. For imine and azine oligomers the fluorescence quantum yields have low values (~0.1), due to the quenching of excited state by nonradiative processes.

In the aryleneimine oligomers series, **T3** and **T4** present a bathochromic shift due to an increase of conjugation length caused by the presence of triphenylamine units, with respect to oligomer having carbazole units (**K3**) (Fig. 2B). Similarly to arylenevinylene oligomers, the bathochromic effect of **T3** besides **T4**, the presence of biphenyl unit caused a blue shifting of the emission maximum to lower values. In the azine oligomers series (**T5** and **K5**), a hypsochromic shift of carbazole-based azine oligomers was observed with emission maximum value located at 428 nm, with respect to

#### Table 1

Optical data for synthesized arylenevinylene, aryleneimine, azine and aryleneethynylene oligomers.

Oligomer	$\lambda_{abs}^{max} (nm)^{a}$	$\lambda_{em}^{max} (nm)^a$	$E_{\rm g}~({\rm eV})^{\rm b}$	$\Phi$
T1	306; 410	467; 500	2.69	0.375
K1	244; 310; 392	434; 461	2.79	0.707
T2	306; 400	463	2.75	0.484
T3	298; 404	498	2.65	с
К3	294; 354; 380	450	2.81	с
T4	297; 398	495	2.73	с
T5	298; 410	493	2.67	с
К5	288; 378	428	2.89	с
T6	306, 388	469	2.82	d
K6	300, 340, 356, 380	405, 433	2.90	d

<sup>a</sup> Determined in diluted CHCl<sub>3</sub> solution.

<sup>b</sup> Obtained from UV–Vis spectra:  $E_{\rm g} = 1240/\lambda_{\rm onset}$ .

<sup>c</sup> <0.1%. <sup>d</sup> Undeter

<sup>d</sup> Undetermined.

triphenylamine-based azine oligomers (Fig. 2C). Ethynylene oligomers show emission maxima at 469 nm (**T6**) and 433 nm (**K6**).

As a conclusion, oligomers containing triphenylamine groups show absorptions and emissions at longer wavelengths as compared with carbazole homologues due to the higher donor character of the triphenylamine group. On the other hand, the order of absorption and emission maxima as a function of  $\pi$ -spacer of arylamine oligomers is:

vinylene > azine > arylenimine > ethynylene

# 3.3. Electrochemical behavior

The cyclic voltammetry was used to investigate electrochemical behavior and to estimate the HOMO levels of oligomers. Oligomers containing triphenylamine units at both ends linked by phenylenevinylene moieties exhibit potentials in the range from 0.0 V to 1.8 V, two anodic peaks located at 0.919 V, 1.113 V for oligomer T1 and 1.053 V and 1.273 V for oligomer T2 (Fig. 3A). These peaks are due to oxidation processes of the triphenylamine units by losing electrons and thus generating cation radicals or dications. On the reverse scanning the oligomers exhibit two reversible cathodic peaks located at 0.973 V and 0.819 V for T1 oligomer and 0.967 V and 0.807 V for T2 oligomer. These cathodic peaks are assigned to reduction processes of the oxidized species that exist at the electrode-solution interface. From the cyclic voltammograms it can be noticed that the presence of the biphenyl central unit linked through vinylene segments by two triphenylamine units, generates more positive values of the oxidation potentials compared to phenyl oligomer one. In addition, the oxidation peaks are very broad and do not have a welldefined shape.

As expected, replacing the vinylene structure with imine segments, the cyclic voltammograms of the corresponding oligomers



Fig. 2. Photoluminescence spectra of arylamine oligomers, recorded in chloroform solution: (A) emission spectra of arylenevinylene oligomers; (B) emission spectra of aryleneimine oligomers; (C) emission spectra of aryleneazine oligomers; and (D) emission spectra of ethynylene oligomers.

are not so different from the previous cases and the curves retain their shape, characteristic to triphenylamine oligomers. Thus, the oligomers T3 and T4, with triphenylamine units at both ends and iminic structures, show in the forward scanning two anodic peaks located at 1.184 V and 1.388 V (for T3 oligomer) and 1.177 V and 1.401 V (for T4 oligomer) (Fig. 2B) which are correlated with the oxidation processes of the triphenylamine units. It can be noticed that the presence of the biphenyl central unit has the same effect as for the vinylene oligomers and the anodic peaks are shifted to positive values of potentials from T3 to T4. From the previous CVs data, it can be said that these peaks can be attributed to the oxidation of triphenylamine units at the ends of the oligomer. On the reverse scanning, the cyclic voltammograms display broad cathodic peaks at 1.069 V for T3 and 1.056 V for T4. These peaks are due to the reduction processes of the oxidized species at the electrode. Moreover, it can be observed that the oxidation and reduction processes of the triphenylamine units occur at more positive values of the potential than vinvlene counterparts and this can be ascribed to electron withdrawing character of the imine segments that is in accord with their electron-deficient nature.

The azine-triphenylamine oligomer exhibits two reversible anodic peaks and two cathodic peaks in the range of 0.0 V-1.800 V. Because the azine structure is not active in the range of positive potentials, these peaks can be attributed only to triphenylamine units. The anodic and cathodic peaks correspond to the oxidation (1.118 V and 1.350 V) and reduction (1.170 V and 1.082 V) processes of the triphenylamine units.

The cyclic voltammograms of **T6** is shown in Fig. 1C, and was recorded in the same conditions as for other previous oligomers. The cyclic voltamograms of the ethynylene–triphenylamine oligomers present only one anodic peak located at 1.152 V. It can be noticed that the oxidation process of triphenylamine groups occurred at positive values than for vinylene oligomers and at

smaller values than for imine oligomers. Thus, it can be concluded that, regarding the oxidation onset values calculated from the anodic sweep, the oxidation processes of the triphenylamine-based oligomers fall in this order:

$$\begin{array}{l} [T1\!<\!T2\!<\!T5]\langle [T6]\!<\![T3\!<\!T4] \\ \mathcal{B}_{ox}^{onset}\!=\!(0.791\,V)(0.824\,V)(0.983\,V)(1.000\,V)(1.048\,V)(1.077\,V) \end{array}$$

From these data it can be conclude that the imine segments being more deficient in electrons, the withdrawing character is more pronounced in oligomers **T3** and **T4** and this leads to a shift of the oxidation processes to more positive values, making the imine oligomers harder to be oxidized comparable with vinylene oligomers.

Taking into account the onset values of the oxidation processes we calculated the HOMO energy levels. As it is well known, the onset oxidation potential observed in CVs is correlated with the highest occupied molecular orbital (HOMO), which corresponds to the ionization potential (IP), while the lowest unoccupied molecular orbital (LUMO) level and electron affinity (EA) were estimated from the onset reduction potential. The HOMO energy values were estimated from the onset potentials of the first oxidation event, after calibration of the measurements against Fc/Fc<sup>+</sup> ( $E_{1/2} = 0.52$  V versus the Ag/AgCl) Because the oligomers are not active on the cathodic scanning CV, the corresponding LUMO levels were obtained by the HOMO values and the energy gaps, which were deduced from the edges of the absorption spectra.

 $E_{\text{HOMO}} = -e(E_{\text{ox}}^{\text{onset}} + 4.28) \text{ eV}$  $E_{\text{LUMO}} = \text{HOMO} - Eg^{\text{opt.}}$ 

All the electrochemical data are summarized in Table 2. The values of HOMO and LUMO levels show these oligomers are good



**Fig. 3.** (A) Cyclic voltammograms of **T1** and **T2** oligomers containing triphenylamine and vinylene structure  $(10^{-3} \text{ M})$ . (B) Cyclic voltammograms of **T3**, **T4** and **T5** oligomers containing triphenylamine and imine structure  $(10^{-3} \text{ M})$ . (C) Cyclic voltammogram of **T6** oligomer containing triphenylamine and etynylene structure  $(10^{-3} \text{ M})$  in CH<sub>2</sub>Cl<sub>2</sub>  $(10^{-3} \text{ M})$ , using Bu<sub>4</sub>NBF<sub>4</sub>, as support electrolyte  $(10^{-1} \text{ M})$ . Scan rate: 50 mV s<sup>-1</sup> between 0.0 V and 1.6 V or 1.8 V, versus Ag/AgCl.

candidates for hole-transporting materials ( $E_{HOMO} = 5.07-5.35$  eV) having a small barrier ( $E_{LUMO} = 2.35-2.67$  eV) for the electron injection from cathodes made from common metals (barium, calcium).

From the structural point of view, carbazole molecules differ from diphenylamines by their planar structure, since it can be further imagined as bonded diphenylamine in *ortho*-positions of phenyl rings, which increase the thermal stability of carbazolecontaining materials. By submitting  $10^{-3}$  M oligomer solution at cyclic voltammetric measurements by swapping the potential applied to working electrode raging in the range of 0.0–1.8 V or 2.0 V, with a scan rate of 50 mV s<sup>-1</sup>, the recorded cyclic voltammograms maintain the characteristic shape of carbazole units (Fig. 4). From the cyclic voltammograms, it can be observed that the oligomer **K1** exhibits three anodic peaks located at 0.881 V, 1.069 V and 1.599 V due to the multiple oxidation processes of carbazole

Table 2			
Electrochemical data	of the	triphenylamine	oligomers

Oligomer E (V)	T1	T2	T3	T4	T5	T6
E <sub>ox1</sub>	0.919	1.053	1.184	1.177	1.118	1.152
E <sub>ox2</sub>	1.113	1.273	1.388	1.401	1.350	1.337
E <sub>ox</sub>	0.791	0.824	1.048	1.077	0.983	1.000
$E_{HOMO}^{a}$ (eV)	5.07	5.10	5.32	5.35	5.26	5.28
$E_{\rm LUMO}^{\rm b}$ (eV)	2.38	2.35	2.67	2.62	2.59	2.46

<sup>a</sup> Determined from the onset of the oxidation peak.

<sup>b</sup> Calculated by the HOMO values and the energy gaps ( $E_{g}^{opt.}$ ).

units, and on the reverse scanning, two cathodic peaks located at 0.973 V and 0.816 V which can be attributed to reduction processes of the oxidized species at the electrode—solution interface. First oxidation peak located at 0.881 V is irreversible and is caused by the formation of the cation radical which follows the typical ECE mechanism, like triphenylamine oligomers. All the electrochemical data recorded for oligomers containing carbazole units are summarized in Table 3.

By repetitive scanning on the positive potentials, multiple cyclic voltammograms for triphenylamine-based oligomers and carbazole-based oligomers in CH<sub>2</sub>Cl<sub>2</sub> solution and using Bu<sub>4</sub>NBF<sub>4</sub> as electrolyte support were recorded. The multiple cyclic voltammograms recorded for triphenylamine oligomers are shown in Fig. 5.

In case of oligomers containing triphenylamine units **T1** and **T2**, the peak potential values are slightly shifted in the positive direction and the reduction potential peak are shifted in the negative direction with increasing of the number of scans. In the case of oligomer with iminic or azinic structure and having triphenylamine units at both ends of the structure, new anodic peaks are formed being located at lower potential values than for oligomer, with increasing the number of the scans. This new peak suggested that new species were formed at the electrode surface and based on the correlation between the potential values of the structural units increased, it could be said that these new peak belong to the polymers that were formed on the electrode surface.

The electropolymerization process and the formation of an electrodeposited thin polymeric films on the Pt electrode, was



**Fig. 4.** (A) Cyclic voltammograms of carbazole-based oligomer with vinyl structure (**K1**) and imine structure (**K2**)  $(10^{-3} \text{ M})$ . (B) Cyclic voltammograms of carbazole-based oligomers with azine (**K5**) and ethynylene (**K6**) structure  $(10^{-3} \text{ M})$  in CH<sub>2</sub>Cl<sub>2</sub>, using Bu<sub>4</sub>NBF<sub>4</sub>, as support electrolyte  $(10^{-1} \text{ M})$ . Scan rate: 50 mV s<sup>-1</sup> between 0.0 V and 1.8 V, versus Ag/AgCl.

Table 3Electrochemical data of the carbazole-based oligomers.

Oligomer E (V)	K1	К3	K5	K6
E <sub>ox1</sub>	0.881	1.207	1.254	0.889
E <sub>ox2</sub>	1.069	1.381	1.501	1.431
E <sub>ox3</sub>	1.599	1.689	1.690	-
Eox	0.792	1.112	1.143	0.80
$E_{\rm HOMO}~(\rm eV)$	5.07	5.39	5.42	5.08
$E_{\text{LUMO}}$ (eV)	2.28	2.58	2.53	2.18

noticed, also, from the increase in peak currents attributed to the monomer-type redox activity (Fig. 5). In all cases, at the end of the repetitive scanning, a polymer film deposited on the Pt plate electrode was obtained. Similar behavior was observed also for carbazole oligomers (Fig. 6).

Having available *para* position on each two phenyl rings of triphenylamine units or 6-position of carbazole ring, after the electron transfer and chemical steps, a dimeric structure can be formed. The cation-radical obtained in the first CV can react with a parent molecule or with another oxidated species generating tetraphenybenzidine or dicarbazolyl structures of oligomers. The redox behavior of triphenylamine molecule was very well studied [31,32]. Based on the literature data it can be assumed that the triphenylamines undergo oxidation processes after which cationradicals are formed. These cations-radicals are not stable and by chemical follow-up reactions tetraphenylbenzidine is formed by tail-to-tail coupling. This step is accompanied by loss of two protons per dimer. When the phenyl groups are substituted at the *para* positions the couple reactions are greatly prevented. In fact, *p*substituted triarylamines often give stable cation-radicals. In the same manner, carbazole cation-radicals dimerizes to dicarbazolyl structures [33].

According to oligomer structures, the electrodeposited polymeric film has different colors, such as; for vinylene oligomers (**T1** and **T2**), the deposited films have a dark-green color. The film



Fig. 5. Multiple scans (10 cycles) for oligomers containing triphenylamine units (10<sup>-3</sup> M) in CH<sub>2</sub>Cl<sub>2</sub>.



Fig. 6. Multiple scans (10 cycles) for oligomers containing carbazole units ( $10^{-3}$  M) in CH<sub>2</sub>Cl<sub>2</sub>.



Fig. 7. DSC scans of triphenylamine-based oligomers (1H, 1C and 2H are: first heating, first cooling and second heating run, respectively). Heating and cooling rate is 10 °C/min, under nitrogen.

deposited on the electrode surface obtained from the electropolymerization of the oligomer **T3** had a bluish green color, and for the film provided from electropolymerization of the oligomer **T4** had a brick-red color. A blue colored film was obtained at the end of the electropolymerization of the oligomer **T6**.

#### 3.4. Thermal behavior

Thermal behavior of the oligomers was investigated using Differential Scanning Calorimetry (DSC). The DSC curves were recorded under nitrogen at a heating and cooling rate of 10 °C/min and Fig. 7 shows the DSc curves for triphenylamine-based oligomers.

With some exceptions (**T2, T4, T6, K6**) the DSC measurements have revealed in the first heating run endothermic peaks associated with melting process. For T1 an endothermic peak was observed at 195 °C which can be assigned to the melting process. During the cooling scan the crystallization process was evidenced by a broad exothermic peak with maximum at 131 °C while in the second heating scan the melting temperature peak appeared at 196 °C. If the sample was rapid cooled, the DSC curve during the heating scan shows the glass transition temperature at 85 °C followed by a crystallization process, and then by melting at 196 °C (Fig. 7). **T3** shows in the first run a melting at 177 °C but by cooling the sample was frozen in glass state and the second heating does not reveal the melting process.

Azine oligomer (**T5**) shows a reversible melting-crystallization during the heating/cooling scans, with two melting temperatures ( $T_{m1} = 219$  °C and  $T_{m2} = 233$  °C), associated with two crystalline states and a crystallization process between 175 and 145 °C at cooling.

A different behavior was observed in the case of T2 that in the heating and cooling scans does not show any melting or crystallization. The sample was obtained as a glass from the synthesis step by precipitation in methanol. If a small quantity of T2 was crystallized from toluene then it exhibits in the first heating run two melting temperature peaks located at c = 209 °C and  $T_{m2} = 225 \text{ °C}$ assigned to the two possible crystalline states [34]. In the second heating run a glass transition temperature was observed at 105 °C but the melting process disappeared due to the oligomer not being crystallized after cooling and remaining in an amorphous state. The absence of crystallization process can be explained by presence of the biphenyl central unit having the two phenyl rings twisted with a dihedral angle to one another due to the sterical hindrances between ortho-hydrogen atoms. In fact all oligomers have a nonplanar configuration but biphenyl moiety introduces a supplementary nonplanarity that improves the morphological stability of the glass state. The nonplanarity of the oligomers explains why the crystallization is a very low-rate process and the formation of glass state by cooling. Similar behavior was observed for the imine and ethynylene homologues T4 and T6 obtained in amorphous states from the synthesis step. The first cooling and second heating runs show the T<sub>g</sub> at 82 °C for **T4** and 103 for **T6** but no crystallization processes were observed. Carbazole-based oligomers have showed similar thermal behavior as compared with triphenylamine homologues, but their corresponding melting and glass transition temperatures are lower.

#### 4. Conclusions

Ten conjugated arylamine oligomers having vinylene, imine or azine isoelectronic structures were have been synthesized by classical polycondensation reactions between aldehydes and bisphosphonate derivatives, diamines or hydrazine or iodide derivatives with 1,4-diethynylbenzene. These oligomers were used as model compounds to obtain information about the corresponding conducting polymer structures, since they have a well-defined molecular structure and can be highly purified using common methods known in organic synthesis.

From the analysis of absorption and emission spectra of these oligomers it can be concluded that the triphenylamine-based oligomers exhibit a bathocromic effect with respect to carbazole-based oligomers, due to a stronger donating ability of the first arylamine group. The introduction of longer spacer as biphenyl unit instead of phenyl unit, led to a blue shifting of the absorption and emission maxima of oligomers. The blue shifting of absorption maxima may be explained by decreasing of conjugation length due to noncoplanarity of the biphenyl central unit. Among  $\pi$ -spacers, phenylenevinylene has the more favourable effect on the absorption spectrum and redox properties.

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