Thin films of arylenevinylene oligomers prepared by MAPLE for applications in non-linear optics

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1. Introduction

Organic compounds show special properties associated with the extended conjugated system of π electrons and the donor–acceptor groups substituted to the aromatic nucleus that generate intramolecular charge transfer properties associated with optical nonlinear phenomena: second harmonic generation (SHG) and two-photon fluorescence (TPF). Triphenylamines [1] and carbazoles [2] are two aromatic amines, which could be used as building blocks for the preparation of conjugated oligomers and polymers, potential candidates for optical non-linear applications such as frequency up-conversion lasing, optical power limiting, 3D fluorescence imaging, 3D optical data storage, 3D lithographic microfabrication and photodynamic therapy [1]. Recent work has emphasised that D–π–D symmetrically substituted organics like those in [1,2] show important high transmission in the visible range, large two-photon absorption (TPA) cross-section and high values of the second order susceptibility [3].

This paper presents the synthesis and characterization of two arylenevinylene oligomers. SHG and TPF optical nonlinear phenomena have been investigated in thin films deposited by Maple Assisted Pulsed Laser Evaporation (MAPLE). The optical properties of the layers have been analysed in correlation with their molecular structure, emphasising the effect on the resultant non-linear optical processes, of the layer morphology which is correlated with the effect of the solvent on the deposition process.

2. Experimental methods

Two arylenevinylene oligomers, 1,4-bis [4-(N,N'-diphenylamino)phenyl]vinyl benzene (P78) and 3,3'-bis (N-hexylcarbazole)vinylbenzene (P13), containing good electron-donating groups (triphenylamine and N-alkylcarbazole) situated at the ends (Fig. 1), were synthesized by Wittig condensation starting from 4-formyltriphenylamine and N-hexyl-3-formylcarbazole with phosphonium salt of 1,4-bis(chloromethyl) benzene. The synthesis of aldehyde derivatives has been presented previously [4,5]. For precipitation was used a fresh solution of sodium ethoxide (C₂H₅ONa). The reaction mixture was stirred at room temperature under nitrogen. The resultant precipitate was filtered...
Fig. 1. $^{1}$H RMN spectra and molecular structures of arylenevinylene oligomers: 1,4-bis [4-(N, N′-diphenylamino)phenylvinyl] benzene (P78); [7.469 (s, Hₐ, 4H), 7.399–7.378 (Hₐ, d, 4H, J = 8.4 Hz), 7.282–7.243 (Hₐ, t, 8H, J = 8.4 Hz), 7.123–7.090 (Hₐ, 8H, J = 7.6 Hz), 7.062–6.96 (He +H₇, m, 12H)]; 3, 3′-bis (N-hexylcarbazole)vinylbenzene (P13); [8.26 (1H, Hj), 7.69 (1H, Hd, J = 8.4 Hz), 8.16 (1H, Hi), 7.50 (1H, Hh), 7.42 (1H, Hg), 7.38 (1H, Hf), 7.23 (1H, He), 7.36 and 7.18 (2H, Hc and Hb), 7.58 (4H, Ha)]; where J: coupling constant, s: singlet; d: doublet; t: triplet; m: multiplet. nH: the number of H which is proportional with the area of the peak.

and washed with ethanol. Yellow powders were obtained after several purifications by precipitation in methanol from a toluene solution.

The structure of the synthesised oligomers was confirmed by $^{1}$H Nuclear Magnetic Resonance (NMR) spectra recorded at room temperature with a Bruker Avance DRX-400 spectrometer (400 MHz) on solutions in deuterated chloroform (chemical shifts are reported in ppm and referred to tetramethylsilane as an internal standard), and Fourier Transform Infrared (FTIR) spectra recorded on pellets of oligomer in KBr with a Digilab-FTS 2000 spectrometer. The UV–Vis and photoluminescence (PL) spectra have been recorded for solutions of oligomers in dichloromethane using a Specord 200 Analytik Jena spectrophotometer and Perkin Elmer LS 55 Fluorescence Spectrometer ($\lambda_{\text{excitation}} = 412 \text{ nm for (P78)}$ and $\lambda_{\text{excitation}} = 396 \text{ nm for (P13)}$).

Oligomeric thin films have been softly, molecule-by-molecule deposited by MAPLE, at room temperature, on different substrates [(0 0 1) quartz, Ti and (1 1 1) Si] that had previously been ultrasonically cleaned in acetone and ethyl alcohol. The quartz substrate was adequate for UV–Vis measurements because it is transparent through UV, Si substrate for PL measurements because it does not give PL signal, and Ti substrate for nonlinear optical phenomenon measurements because it does not give SH and TPF signals. The targets were obtained by liquid nitrogen freezing of the solutions prepared by dissolving the oligomers in a highly volatile and light absorbing solvent [chloroform (CHCl₃) or dimethylsulphoxide (DMSO)] and subsequently ultrasonically homogenised at 40 °C. The main part of the deposition system was the KrF excimer laser, Coherent CompexPro 205 (λ = 248 nm, τFWHM = 25 ns repetition rate = 5 Hz; 10 Hz). Short pulse laser irradiation generates the vaporization of the frozen target and, while the solvent molecules are removed by the pumping system, the organic molecules deposit on the substrate situated a distance of 4 cm from the target. Details about the experimental configuration have been given in previous papers [6–9]. The variable experimental parameters are: pressure ($2 \times 10^{-2}$ to $2 \times 10^{-1}$ mbar), fluence (145–250 mJ/cm²), and number of pulses (5000–60,000).

The MAPLE thin films have been characterised by UV–Vis and PL spectroscopy using a Double beam CINTRA 10e GBC Spectrophotometer and Spectrofluorimeter Edinburgh Instruments F-900
Fig. 5. (P78) oligomer SEM images [a: quartz/chloroform; c: quartz/DMSO; d: Ti/chloroform] and AFM [b: Ti/chloroform]: root-mean-square (RMS) = 107 nm and roughness average (RA) = 85 nm.

Fig. 6. (P13) oligomer SEM images [a: quartz/chloroform; c: quartz/DMSO; d: Ti/chloroform] and AFM [b: Ti/chloroform]: root-mean-square (RMS) = 33 nm and roughness average (RA) = 25 nm.
Results and discussion

The $^1$H NMR analysis (Fig. 1) revealed that both oligomers have trans-arylenevinylene structure, which is confirmed by the absence of any peaks in the 6.5–7.0 ppm region of the spectra where usually the peaks assigned to cis –CH– group in cis stilbene are situated. The signals assigned to the protons of triphenylamine and carbazole units were observed in the region 6.96–7.47 ppm and to the trans-vinyl protons, which are intercalated between the aromatic signals, at 7.38–7.40 ppm (P78) and 7.16–7.20 ppm (P13). Oligomer (P13) due to the long alkyl group attached as a side chain to the nitrogen atom provides a greater tendency of trans-formation in the Wittig reaction, because of the high steric hindrance. The FTIR spectra (Fig. 2) have shown the characteristic bands of the chromophoric groups in oligomers: 1590–1598 cm$^{-1}$, 1490–1492 cm$^{-1}$ and 1505–1586 cm$^{-1}$ attributed to ring in-plane bending vibrations of the phenyl ring mono-substituted ($\nu_{\text{C–C}}$); 1505–1586 cm$^{-1}$ attributed to the phenyl rings (C–C); 1316–1332 cm$^{-1}$ and 1030–1190 cm$^{-1}$ corresponding to the normal vibration with significant contributions from the C–N stretching coordinates; 695–697 cm$^{-1}$ corresponding to the out-of-plane (wagging) vibration of the hydrogen atoms attached to the phenyl rings; 747–752 cm$^{-1}$ due to the corresponding out-of-plane (puckering) vibration of the phenyl rings; 814–827 cm$^{-1}$ attributed to the deformation vibrations of the C–H bonds of the p-substituted phenyl rings. Both oligomers have trans-arylenevinylene structure which is also confirmed by characteristic IR absorption peaks at 960–962 cm$^{-1}$ corresponding to the out-of-plane bending vibration of HC=CH.

The electronic structure of the arylenevinylene oligomers was investigated by UV–Vis and PL spectroscopy (Fig. 3). Several absorption peaks could be observed in the wavelength range from 225 to 500 nm, while no linear absorption was observed beyond 450 nm. The oligomers have appropriate values for absorption and emission peaks but in the case of carbazole oligomer (P13), the peaks are much broader. The absorption peaks at 412 nm (P78) and 369 nm (P13) can be assigned to the electronic $\pi$–$\pi$ transition of the conjugated backbone. Strong blue–green fluorescence in diluted solution were obtained with good yield of 94%, situated at $\lambda = 470$ nm for (P78) and 95% situated at $\lambda = 464$ nm for (P13).

These spectra were compared with the UV–Vis and PL spectra of thin films prepared from the same monomers (Fig. 4). The thin films of (P78) show the same shape (independent of solvent) of the absorption edge situated between 200 and 400 nm with two local maxima, but this feature was not seen for (P13) thin films. The optical transitions are strongly affected by the inherent intramolecular electronic interactions and strong polarization interactions with the surrounding medium [10], which are favoured in oligomer (P78) characterized by a higher conformational flexibility compared to oligomer (P13). The PL intensity, for the same $\lambda_{\text{excitation}} = 350$ nm, are stronger and broader for MAPLE oligomers films deposited from CHCl$_3$. Independent of solvent, the emission peak is weaker for (P13) compared to (P78), but the peak of (P13) in DMSO is split into two maxima situated at 490 nm and 525 nm. The peak of the (P78) film shows a slight red shift (480–490 nm) compared with that of (P78) powder in dichloromethane, which is mainly attributed to the presence of strong polarization interactions, especially in the solid state due to the large polarizabilities of the $\pi$ conjugated chain.

SEM and AFM images of the MAPLE thin films have revealed a significant roughness [higher for (P78)] generated by the presence of grains of typical dimension up to 200 nm, and larger scale structures with spherical morphology. The oligomer–solvent matrix droplets, which have appeared in the disintegration of the heated target favours the inclusion of the volatile solvent in the oligomer rich surface layer generating the wrinkled oligomer structures [11]. The morphologies of the (P78) oligomer layers deposited on quartz and Ti using chloroform are not significantly different, and are characterized by spheres with different dimensions randomly distributed in the layer. The (P78) layer deposited on quartz using DMSO has shown a morphology characterised by a lower density of spherical structures (Fig. 5). The (P13) layers deposited on quartz substrates have shown a grainy morphology characterized by the presence of randomly distributed grains with a higher density in the layer deposited using DMSO. The (P13) layer deposited on Ti substrate using chloroform has shown a morphology characterised by a lower density of large spheres (Fig. 6).

We have applied a simple technique which uses SHG induced by the ultra-intense focused beam of a femtosecond laser, in a reflec-
tion configuration, to compare the second-order NLO coefficient of the (P13) and (P78) oligomer films deposited on Ti substrate. The Ti substrate has no contribution to the nonlinear optical phenomenon. The simplified expression for the SHG signal intensity is given by \( I(2\omega) \propto \left( \frac{\chi^{(2)}}{US(2)} \right)^2 P^2(\omega) \) [12] (where \( P \) is the average power of the pulsed laser). Thus the slope of the plot \( I(2\omega) \) versus \( P^2(\omega) \) is a measure of the nonlinear optical behavior of the material (Fig. 7). We conclude that the two oligomers are similar from the point of view of the second-order NLO coefficient for \( P_{\text{laser}} < 100 \) mW. The deviation from linear dependence for \( P_{\text{laser}} > 100 \) mW can be explained by the thermally induced conformational changes of side chains generated by the absorbed laser radiation, that involves reorientation of the dipoles and changes in the polarizability of the materials. The \( z \)-scan and \( x \)-scan representations for (P13) have shown that TPF broad band with a peak around 650 nm is more intense inside the samples confirming a volume process which is not affected by the layer surface morphology. On the contrary, SH is stronger at the surface of the sample (Fig. 7) and could be influenced by the morphology which is determined by the solvent selected for target preparation.

4. Conclusions

This paper presents a study on the optical properties of as-synthesised and MAPLE deposited thin films of 1,4-bis \([4-(N,N'-diphenylamino)phenylvinyl] \text{benzene and 3,3'-bis}\ (N\text{-hexylcarbazole})\text{vinylbenzene oligomers. The trans molecular structure of the two arylenevinylene oligomers was confirmed by the characteristic absorption peaks situated between 960 and 962 cm}^{-1} \text{in the FTIR spectra and by the absence of any peaks assigned to cis} \,-\,\text{CH=CH-- in the 6.5--7.0 ppm region of the} \,^1\text{H NMR spectra. UV--Vis and PL measurements have confirmed that the chemical structures of the oligomers have been preserved during the MAPLE deposition process. The thin films of both oligomers deposited on Ti substrates by MAPLE have shown SHG.}

We have obtained values nearly equal of the second-order NLO coefficients for both (P13) and (P78) thin films deposited on Ti at laser power < 100 mW. This behaviour is independent of the solvent used for the preparation of the targets. A saturation of the SH was observed at laser powers higher than 100 mW generated by changes in polarizability, which are associated with thermally induced conformational changes of the oligomer molecules. We have also observed variations in the SH and TPL intensities which have depended on the position on the surface and in the depth of the (P13) film.

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