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Synthesis and characterization of a new alternating copolymer containing quaterphenyl and fluorenyl groups

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Abstract

An alternating copolymer was synthesized by Suzuki reaction from 4,4′-dibromo-*p*-quaterphenyl (PPP oligomer) and 9,9-dioctylfluorene-2,7-diboronic acid in good yield (84%). The copolymer is partially crystalline, readily soluble in organic solvents, presents high fluorescence quantum yield (85.6%) and high thermal stability. The copolymer absorption as well as the emission spectra are red shifted compared to those of monomers. Ultrafast time-resolved fluorescence experiments on the copolymer were carried out and confirmed the results obtained from stationary experiments. The copolymer fluorescence decay is found to be bi-exponential with fluorescence lifetimes of 297 ± 6 ps and 942 ± 5 ps.
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1. Introduction

In recent years various synthetic approaches have been developed to prepare new polymers with high photoluminescence (PL) efficiency and good thermal stability. The conjugated polymers have shown to present considerable advantages over the well-established inorganic electroluminescent materials and organic dye molecules since they can be deposited on large areas by solution coating.

An interesting potential material in optical applications is poly(*p*-phenylene) (PPP) because of its band gap with emission in the blue region and good thermal stability and photoluminescence properties [1,2]. However, this type of polymer is quite insoluble, although it is believed that soluble oligomers containing four aromatic rings present almost the same characteristics as the polymer itself, at least concerning the vibrational spectra [3]. Thus, efforts have been directed to prepare soluble PPP modified derivatives [4,5]. Besides, *p*-quaterphenyl can be used as laser dyes [6]. Poly(fluorene)s and copolymers are an attractive class of light emitting polymers due to their high photoluminescence (PL) quantum yields, thermal stability and good solubility [7]. The most often claimed application of poly(fluorene)s is in light emitting diodes (LEDs). Devices can be easily fabricated using these copolymers, which present blue emission and can have improved performance by energy transfer between the components with different band gaps [8]. The 9-position of the fluorene offers the ability to control interactions among chains through functionalization, leading to tailored electrical and optical properties. For instance, blue-emitting fluorinated fluorene-containing copolymers were successfully synthesized with excellent thermal stability, reduced turn-on voltage and enhanced electroluminescence (EL) [9,10].

Poly(aryl ether)s consisting of alternating isolated *p*-quaterphenyl and fluorene units have been reported to be easily
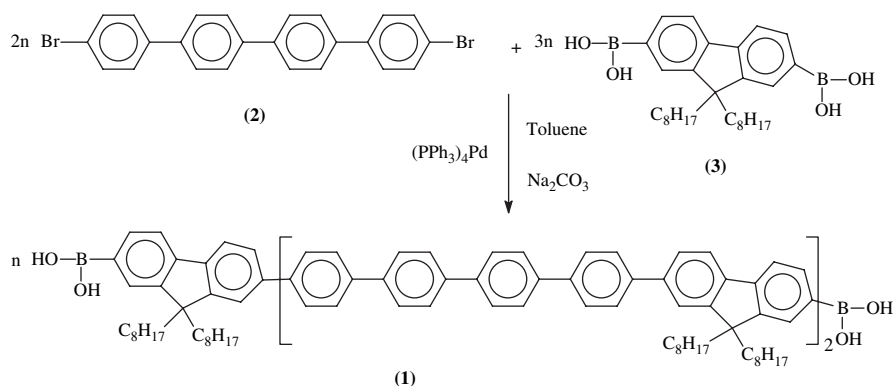

Fig. 1. Polycondensation by Suzuki reaction of 4,4′-dibromo-*p*-quaterphenyl and 9,9-dioctylfluorene-2,7-diboronic acid.

dissolved in organic solvent and exhibit high PL and good thermal stability up to 500 °C in nitrogen atmosphere [11,12].

The Suzuki reaction is a versatile reaction involving carbon−carbon bond formation in the presence of a palladium catalyst, thus a compound containing a borate group and another organo-halide compound [13,14] are easily reacted. This reaction offers several additional advantages, since it is not affected by the presence of water and tolerates a wide range of functional groups. Besides, the inorganic by-product of the reaction is non-hazardous and can be removed easily from the reaction mixture, which turns out to be suitable not only in laboratory scale, but also in industrial production processes. There are many electroluminescent polymeric materials synthesized by this technique [15].

In this work we present the synthesis and characterization of a new alternating copolymer (**1**) synthesized (Fig. 1) from 4,4′-dibromo-*p*-quaterphenyl (**2**) and 9,9-dioctylfluorene-2,7-diboronic acid (**3**). We believe that the copolymer (**1**) may present better electronic conductivity compared to the poly(aryl ether)s consisting of alternating isolated *p*-quaterphenyl and fluorene units [11,12], while photoluminescence and thermal properties may remain comparable.

2. Experimental

2.1. Starting materials

All reagents were purchased from commercial sources (Aldrich or Acros) and used without further purification, except when specified. The 4,4′-dibromo-*p*-quaterphenyl (**2**) was prepared as described in the literature [3]. The solvents used for chemical reaction were dried under nitrogen.

2.2. Characterization

[1]H Nuclear magnetic resonance spectra (200 MHz) were recorded using a Bruker AC-200 spectrometer with deuterium chloroform (Aldrich) as solvent and tetramethylsilane (TMS) as internal reference. FTIR spectra were performed using a Nicolet Avatar 320© spectrometer. Samples were dissolved in chloroform and cast on KBr plates and evaporated to dryness before collecting transmission spectra from 450 to

4500 cm^{-1} at 4 cm^{-1} resolution (32 scans). Elemental analyses were carried out using a Perkin Elmer Elemental Analyzer 2400 CHN. Raman scattering spectra were recorded by a Bruker RFS100 spectrometer with an excitation wavelength λ_{exc} set at 1064 nm. Wide-angle X-ray diffraction (WAXS) measurements were carried out using a D5000 Siemens diffractometer with Cu Kα line ($\lambda = 1.54$ Å) radiation on polymer films in a conventional horizontal configuration using a scan rate of 2°/min with 2θ ranging from 2° to 60°. The UV absorption spectra were collected on a Varian equipment, Cary 50 Conc. Samples were dissolved in chloroform and the solution was poured into a 10 mm square quartz cell. The transmission spectrum was collected from $\lambda = 200−600$ nm. The photoluminescence spectra (PL) in solution were determined using a Varian Eclipse fluorescence spectrophotometer. Samples were dissolved in chloroform and subjected to irradiation at the absorption maximum observed by UV spectroscopy and the emission spectra were collected accordingly. Photoluminescence measurements were also done in solid state. The material was dissolved in chloroform and the film was deposited as substrate by casting on a glass plate. The sample was treated in an oven for 5 min under vacuum. The measurements were performed after treatments at 25, 50, 100 and 150 °C. Ultrafast photoluminescence experiments were carried out with the recent regenerative amplified femtosecond laser system installed in Nantes (Hurricane X). This setup delivers 100 fs pulses at 1 kHz, 800 nm and 1 W. Solid-state polymer samples were excited at $\lambda_{exc} = 400$ nm (3.1 eV) by the frequency-doubled Ti:sapphire laser line sent into a single harmonic generation box (SHG). The remnant 800 nm laser signal in the output laser beam was filtered with an Ekspla colored glass filter No C3C21. Neutral density filters allowed a SHG pump power decrease by a factor of 10^2. The mean pump power for luminescence was then set at about 1 mW. The transient signals were spectrally dispersed into an Oriel MS260i imaging spectrograph (150 grooves/mm, $f = 1/4$), designed to minimize stray light with high spectral resolution. MgF$_2$ lenses of 50 mm focal length were used to collect the signal at the entrance slit of the spectrograph (30 µm). The laser signal was partially directed to the spectrograph by using an Ekspla colored glass filter No JC11, to provide a spectral calibration reference. Finally, the time-resolved emission

spectra were spatio-temporally detected with a high dynamic range Hamamatsu C7700 streak camera of temporal resolution lower than 20 ps. The streak images were stored by an ORCA II CCD camera (1372 × 1024 pixels) kept at −60 °C. The entrance slit of the streak camera was set as 60 μm. Jitter correction was achieved using the Hamamatsu software. Acquisitions were made without pixel binning. The trigger and the temporal windows of the streak camera sweep were directly controlled by the out-synchronizer of the Hurricane. In addition to the transient "operate" mode, the streak camera was also used in focus mode in order to acquire stationary PL spectra in the same operating conditions, to compare them with spectra taken on continuous wave fluorescence spectrophotometers. In operate (focus) mode, the acquisition parameters were set at gain = 63 (3) with 50 (10) accumulations during 500 ms for the analogical integration.

2.3. Synthesis of the alternating copolymer

In a dry box, 0.502 g (1.05 mmol) of 9,9-dioctylfluorene-2,7-diboronic acid (Aldrich 96%), 0.327 g (0.705 mmol) of 4,4′-dibromo-p-quaterphenyl, and 0.012 g (0.01 mmol) of P(Ph₃)₄Pd (Acros 99%) were placed in a 50 mL three-necked round-bottom flask with 15 mL of toluene under argon atmosphere. A pressure-equalizing dropping funnel with 7 mL of Na_2CO_3 solution (2 M) and a reflux condenser were attached to the reaction flask, in which the mixture was allowed to react under argon atmosphere and magnetic stirring for 24 h in a dark place. Thereafter, the solution was filtrated and washed with toluene and water and, finally, dried over $MgSO_4$. The solvent was evaporated to dryness and the white residue was characterized as the copolymer (1). $\eta = 84\%$. ^{1}H NMR (CDCl₃): $\delta = 7.8$–7.2 (m, 22H, Ar–H), 1.98 (m, 4H, CH₂), 1.08 (s, 20H, CH₂), 0.81 (m, 6H, CH₃). $C_{135}H_{156}B_2O_4$: Calcd. C 86.97, H 8.43, B 1.16, O 3.43. Found C 83.57, H 8.68.

3. Results and discussion

The Suzuki reaction showed to be suited for the alternating copolymer preparation in good yield (84%) because of its non-complexity. Some product lost is believed to occur during purification due to the good solubility of the product, as a low molar mass oligomer having alkylated fluorene was prepared. In this work the relative amount of monomers was set as 2 mol of 4,4′-dibromo-p-quaterphenyl to 3 mol of 9,9-dioctylfluorene-2,7-diboronic acid, which may result in a boronic acid-terminated oligomer, presenting a calculated $M_n = 1860$ g mol^{-1}, as depicted in Fig. 1. The prepared oligomer will be further reacted to produce a block copolymer bearing electronic charge carrier segment, n and/or p type, along with high PL chromophores, aiming at multifunctional LEDs' active layer.

The ^{1}H NMR results were coherent with the copolymer formation. Both the NMR spectra of 9,9-dioctylfluorene-2,7-diboronic acid and copolymer have shown a tiny broad peak at 4.5–5 ppm, which was not possible to be correctly quantified. Although the presence of that peak indicates boronic OH

in the copolymer, we were not able to calculate the copolymer chain length by NMR.

Size exclusion chromatography of different copolymer samples was carried out in THF solution and the results were compared to the calibrations with 4,4′-dibromo-p-quaterphenyl and 9,9-dioctylfluorene-2,7-diboronic acid, which led to the conclusion that the copolymer samples were composed by a mixture of oligomer chains, with molar masses ranging from 2500 to 4200 g mol^{-1}, the main peak being centred at 2820 g mol^{-1} and a second small peak at 850 g mol^{-1}. Assuming a molar mass close to 690 g mol^{-1} for the constitutive unit quaterphenylene–dioctylfluorenylene, a rough calculation gives a degree of polymerization of 4 units for the main peak. Additionally, it can be deduced that oligomer lengths fluctuated from 3 to 6 units, a little bit longer than the expected values of 2.5–5 units calculated from the reactant molar ratio, according to Carothers equations for stepwise polymerization.

Fig. 2 shows the infrared spectra of the monomers (9,9-dioctylfluorene-2,7-diboronic acid and 4,4′-dibromo-p-quaterphenyl) and that of the synthesized alternating copolymer. The three spectra show distinct functional group absorptions, which can be easily correlated to the copolymer formation.

In Fig. 2, spectrum (a) shows the disappearance of the bands at 1320 and 1350 cm^{-1}, characteristics of the B–O bonds in the boronic group as in spectrum 2 (b), which is an evidence of the formation of the copolymer since boronic groups are removed during the polycondensation reaction. Furthermore, in spectrum (a), both aromatic and aliphatic C–H stretching absorptions are observed at 3029 and 2850–2930 cm^{-1}, respectively, along with the aromatic C=C stretching at 1464 cm^{-1} and aromatic C–H out of plane rocking at 814 cm^{-1}.

Fig. 3 presents the Raman scattering spectrum of the alternating copolymer obtained by the Suzuki reaction. This spectrum is very similar to that observed for PPP [16], the phenyl group vibration modes are observed at 1599, 1215 and 1279 cm^{-1}, as described in the literature [17]. The main difference, compared to PPP, is observed at 2895 cm^{-1}, where
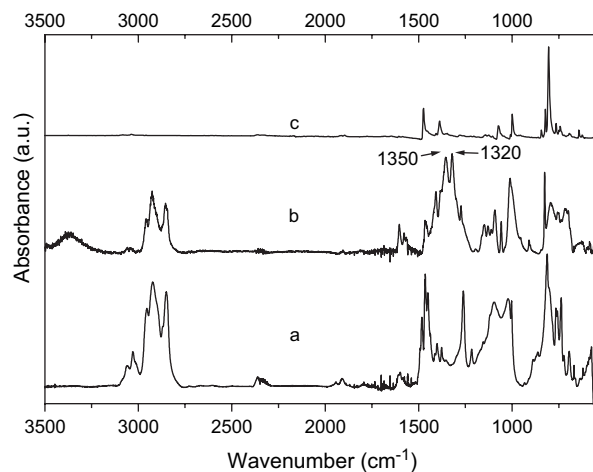

Fig. 2. Infrared spectra of (a) alternating copolymer (1), (b) 9,9-dioctylfluorene-2,7-diboronic acid (3) and (c) 4,4′-dibromo-p-quaterphenyl (2).
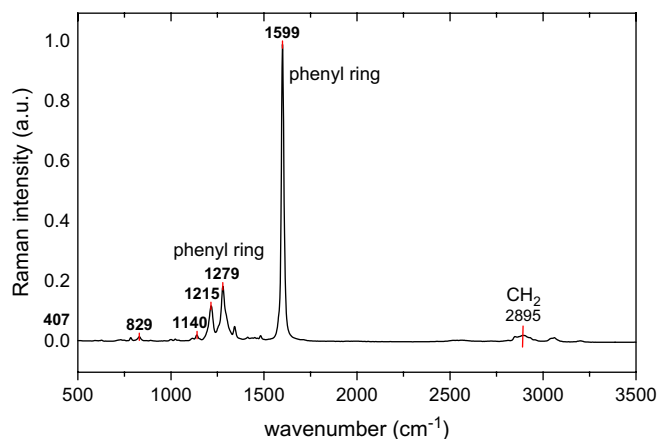
Fig. 3. Raman spectra of an alternating copolymer sample (excitation wavelength: 1064 nm; resolution: 4 cm^{-1}).

a broad band corresponding to the CH$_2$ vibration mode, reveals the presence of 9,9-dioctylfluorenyl groups.

By WAXS (Fig. 4), the alternating copolymer was shown to be semicrystalline, although the crystalline fraction remained quite low. One broad correlation peak is observed at $d = 13.9$ Å and another one is convoluted with the 4.55 Å peak, and is attributed to the disordered arrangements of the amorphous polymer chains. Three sharp peaks at $d = 3.20$, 3.95 and 4.55 Å are attributed to the crystalline arrangement. The observed diffraction peaks might be due to the π-stacking of phenyl rings [18] of the quaterphenyl segments, which means that the stacking planes might be arranged perpendicular to the polymer chain axis [18,19]. PPP powder was reported to be amorphous [20], however, thin films and doped powder have been reported to present orthorhombic or hexagonal crystalline structure, with lattice parameters depending on the presence and nature of side alkyl groups or doping electrolyte [18,20].

Fig. 5 shows the optical absorption and the photoluminescence emission spectra of alternating copolymer (**1**), 9,9-dioctylfluorene-2,7-diboronic acid (**3**) and 4,4′-dibromo-*p*-quaterphenyl (**2**) in CHCl$_3$. In the absorption spectrum, a red
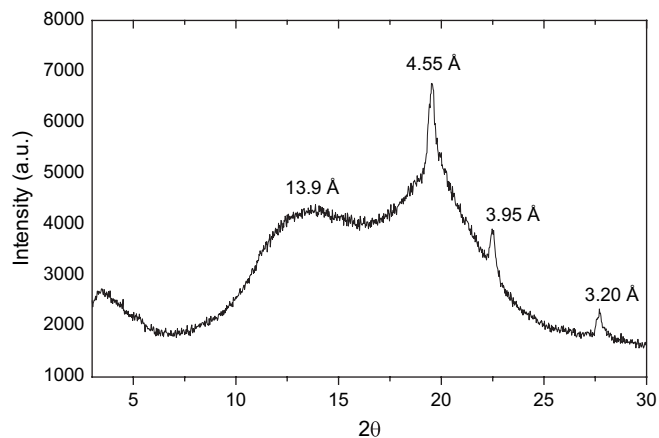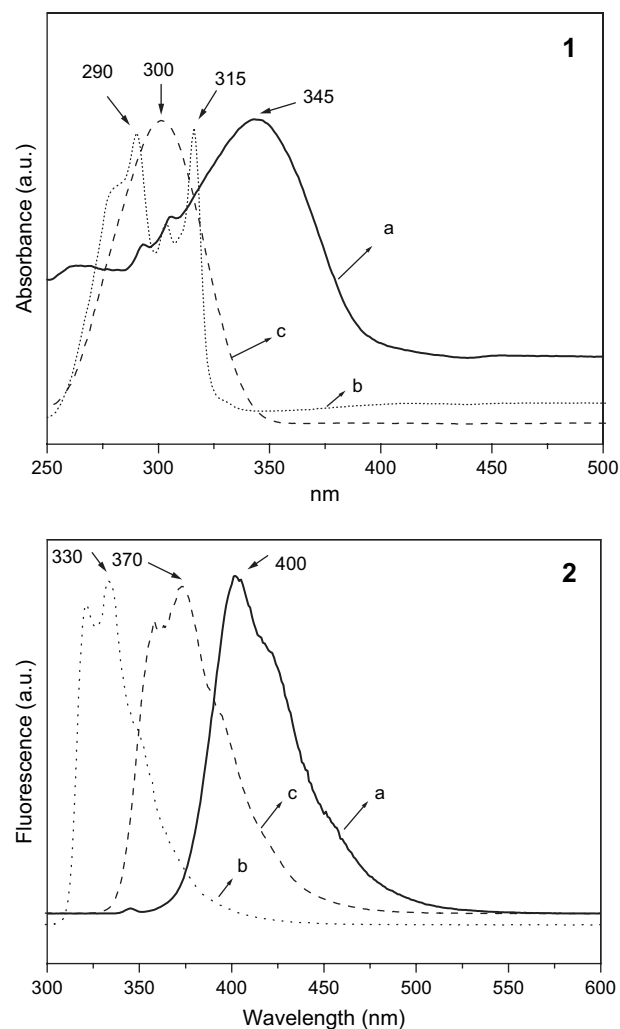

Fig. 5. (1) Absorption spectra and (2) fluorescence emission spectra in CHCl$_3$ of (a) alternating copolymer (b) 9,9-dioctylfluorene-2,7-diboronic acid and (c) 4,4′-dibromo-*p*-quaterphenyl.

shift is observed for the copolymer, with a maximum peak at 345 nm, compared to 300 nm for 4,4′-dibromo-*p*-quaterphenyl and 315 and 290 nm for the diboronic acid. This result also indicates the polymer formation, as an optical absorption different from the starting materials has been observed.

As the light emission process by electroluminescence is the same as by fluorescence — the difference being that the exciton is created by electrical excitation rather than by light irradiation — the measurement of the fluorescence quantum yield allows the evaluation of the role played by fluorescence among the competitive exciton deactivation processes involved. Such an approach allows a rapid screening of the potential chromophores.

The luminescence quantum yield was measured using quinine sulfate as standard [21]. Among the compounds used as standard, its quantum yield is believed to be one of the best known; it is not oxygen quenched; exhibits little concentration quenching; there is no significant overlap between its absorption and emission spectra and it is stable in solution. An improvement of the quantum yield to 85.6%, for the

Fig. 4. X-ray diffraction curve of alternating copolymer sample.

copolymer, against 69.3%, for the 4,4′-dibromo-*p*-quaterphenyl, was observed. In addition, the copolymer presented the emission wavelength shifted slightly to the visible region, compared to those of the starting monomers, and the maximum was centred at 400 nm.

The thermal stability of the copolymer was checked by thermogravimetry (TGA) under nitrogen atmosphere. The temperature was increased from 30 to 600 °C at 20 °C/min. It is interesting to mention that the copolymer presented no weight loss until 250 °C. The TG curve of the copolymer was characterized by two decomposition steps, with onset at 260 and 380 °C, after which the sample remained stable until 600 °C, when approximately 50% of its starting weight still remained. Comparatively, PPP, which thermal volatilisation initiates at 100 °C, has been observed to present at 250 °C a weight loss of 20% and at 600 °C, 65% [22]. Moreover, TGA of 4,4′-dibromo-*p*-quaterphenyl showed constant weight up to 250 °C, with subsequent continuous decomposition up to 440 °C, when 100% of weight loss was reached.

Fig. 6 shows the photoluminescence spectra of solid-state copolymer after annealing at different temperatures. All spectra show the same shape, there is no additional band or any deformation of the existing bands due to the thermal treatment. In fact, it is possible to observe a little increase in the intensity with the increase in the annealing temperature. In contrast to the solution spectrum, it is possible to observe three bands at 417, 440 and 470 nm in the solid-state spectrum. The peak at 417 nm is red shifted compared to the solution spectrum (at 400 nm). This shifting is usual and may be caused by stronger intermolecular interactions in the solid state.

This set of experiments shows that this new material is thermally stable and has potential to be used in displays up to 150 °C.

Fig. 7 displays the 3D camera streak image of the ultrafast photoluminescence recorded on the 5 ns time window (5.146 ps/pixel) for copolymer powder pressed onto a silica glass. The spectral range extends over 303.9795 nm
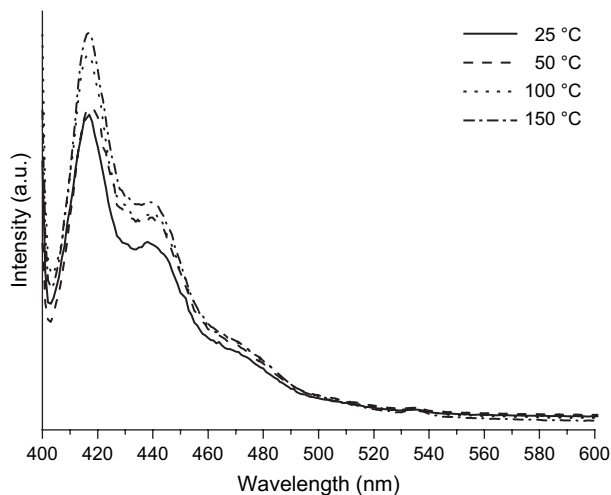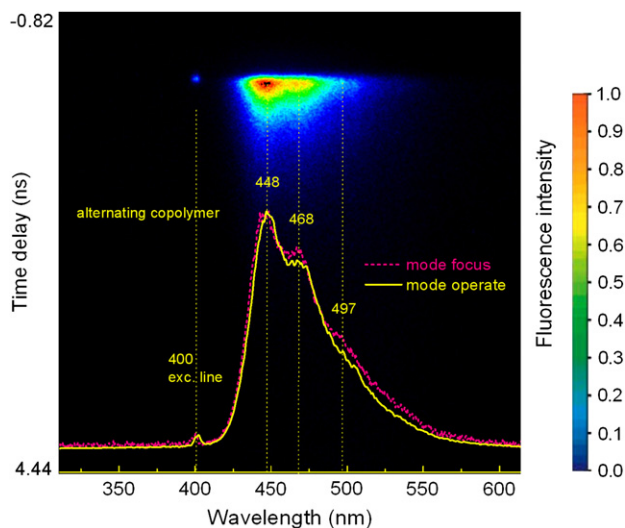

Fig. 7. Streak camera image of the ultrafast fluorescence emission of the alternating copolymer obtained with the setup of Nantes. The region of interest is 1024 × 1024 pixels in size (no pixel binning). The fluorescence intensity increases from blue color to red color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.) The fluorescence is normalized to the maximum intensity by the look-up-table tool of the acquisition software. The solid curve is the time-integrated fluorescence of the raw streak image, and the dashed curve is the stationary spectrum obtained in focus mode. The beginning of the streak camera sweep has been offset at −0.82 ns corresponding to a laser pulse starting at $t = 0$ ns.

(0.297 nm/pixel). In the color scale, the PL intensity increases from blue to red regions. The left spot on the image corresponds to the femtosecond laser excitation at 400 nm. The solid curve shows the transient PL spectrum extracted from the time-integrated intensity on the whole image acquired in operate mode. The dashed curve is the PL spectrum acquired in focus mode, this is in fact the steady-state PL spectrum obtained for the 400 nm excitation. The two spectra match almost perfectly with one another. The well-defined peak structure may be ascribed to vibronic features as observed for the steady-state PL spectra (Figs. 5 and 6) recorded for $\lambda_{\text{exc}} = 345$ nm in solution and 410 nm in solid state, respectively. The Gaussian decomposition of these spectra yields 3 components located at 445, 469 and 485 nm, in agreement with the spectrum of Fig. 6. A component at about 420 nm was also observed in time-resolved experiments when a very low amount of copolymer dust was rubbed on silica glass (not shown here).

The PL intensity decay corresponding to this image is plotted in Fig. 8 on a logarithmic scale. It can be seen that this decay is non-linear. This suggests that more than one excited electronic level is involved in the PL process. We succeeded to reproduce well the kinetics with two-level coupled populations decaying exponentially according to the following rate equations:

$$\frac{dn_1}{dt} = G(t) - n_1\beta_1$$

$$\frac{dn_2}{dt} = n_1\beta_1 - n_2\beta_2 \tag{1}$$

Fig. 6. Fluorescence spectra of solid-state copolymer after annealing at different temperatures.
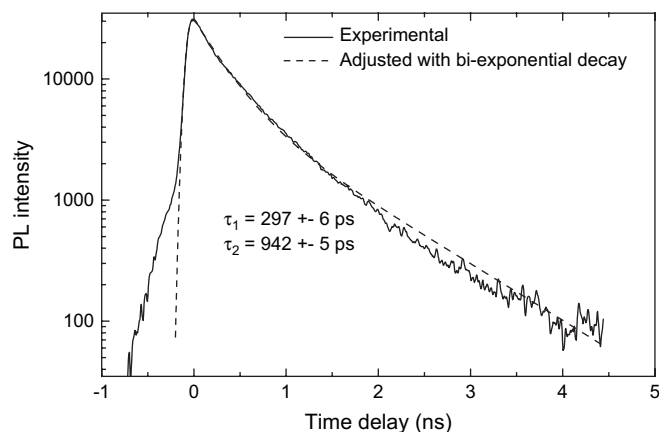
Fig. 8. Ultrafast fluorescence decay in semi-logarithmic scales of the alternating copolymer extracted from Fig. 7. The dashed line is the experimental data fit to the bi-exponential model given by Eq. (1) (see text).

where n_1 and n_2 are the excited populations, and β_1 and β_2 are their inverse lifetimes $(1/\tau)$. $G(t)$ is the Gaussian exciton generation rate convoluted by the apparatus function of the setup. Using, for example, formal calculus via a Maple code, one can analytically solve Eq. (1). The solution for this equation is given in the literature [23]. The fit to the data is readily achieved by using the non-linear curve-fitting tool of the Origin software. We find $\tau_1 = 297$ ps and $\tau_2 = 942$ ps. These lifetimes lie in sub-nanosecond range that is quite fast. This indicates that probably the PL dynamics is mainly driven by the fast recombination of singlet excitons. Also, we note that the transient PL intensity reaches a much higher value (around 31 000 counts) than that recorded for poly-*p*-phenylene–vinylene compounds on the same setup. This is in agreement with the high quantum yield obtained from stationary spectra.

The ultrafast photoluminescence of 4,4′-dibromo-*p*-quaterphenyl in solid state is given in Fig. 9, and the corresponding
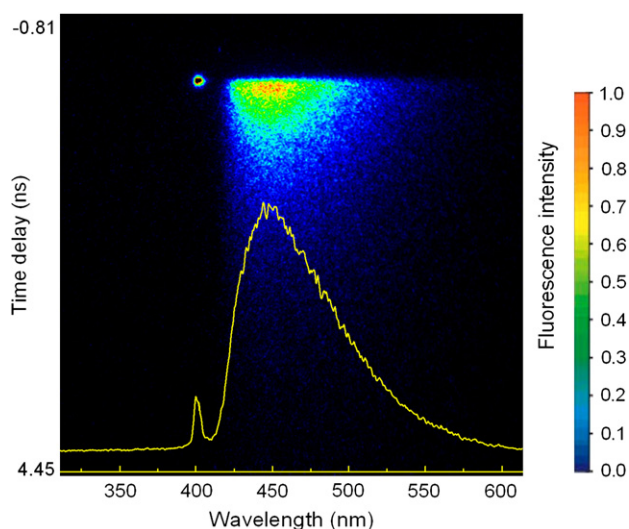

Fig. 9. Streak camera image of the ultrafast fluorescence emission of 4,4′-dibromo-*p*-quaterphenyl. The curve is the time-integrated fluorescence of the raw streak image.
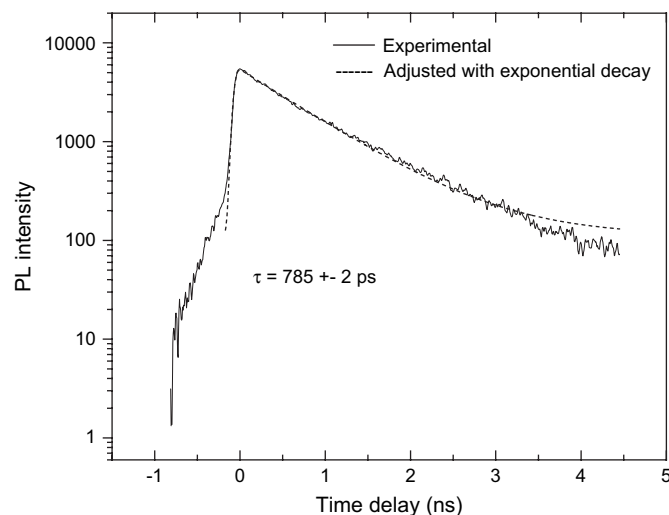

Fig. 10. Ultrafast fluorescence decay in semi-logarithmic scales of 4,4′-dibromo-*p*-quaterphenyl extracted from Fig. 9. The dashed line is the experimental data fit to the mono-exponential model given by the first Eq. (1) (see text).

fluorescence decay is shown in Fig. 10. The maximum fluorescence for this laser excitation is located at 448 nm. The signal looks similar to that of the alternating copolymer which means that the presence of quaterphenyl groups in the copolymer is confirmed. However, no vibronic structures are observed at the photon fluence used. In addition, the PL intensity decay is mono-exponential, in contrast to that of the copolymer. The exciton lifetime is 785 ps. Indeed, one can note by comparing the two streak images that the fluorescence of the copolymer is much faster than that of the quaterphenyl compound. Therefore, the ultrafast PL experiments provide an additional substantiation so that a new polymer synthesis has been achieved by our method.

Both the alternating copolymers of fluorene and *p*-quaterphenyl featuring ether linkage or carbon–carbon bond presented good thermal stability and high fluorescence. UV–vis absorption and emission spectroscopies have shown blue shifted spectra for the present copolymer relative to its ether version [11,12], $\lambda_{max,abs} = 345$ nm and $\lambda_{max,em} = 400$ nm against $\lambda_{max,abs} = 385$ nm and $\lambda_{max,em} = 423$ nm, respectively. However, the differences in wavelength are probably due to the intramolecular conjugation extension, which is associated to the polymer molar mass. The oxygen connected copolymer version [11,12] presented longer chains (about $10\times$) compared to the present whole conjugated oligomer. It is possible that the new copolymer may present higher conductivity due to the aromatic π electron resonance along the chains, nevertheless that improvement would be only observable in polymers with equivalent chain lengths. Another important point is that the Suzuki reaction presents high specificity allowing product molar mass control and segmented copolymer preparation, and reactions are carried out in mild conditions, while production process scale up can be readily achieved due to the straightforward product purification procedure.

4. Conclusion

The Suzuki reaction was shown suitable and quite specific for preparation in good yield of an alternating copolymer starting from *p*-quaterphenyl and alkyl-fluorene derivatives. The copolymer samples, prepared so far, are composed of a mixture of oligomers showing polymerization degree close to the calculated values. The copolymer showed high solubility in chloroform, due to the alkyl substitution at the fluorene 9-position. UV–vis spectroscopy as well as the emission photoluminescence spectroscopy of the copolymer showed red shifted spectra, compared to those of the monomers. Transient photoluminescence experiments of the copolymer evidence a high-intensity PL profile agreeing with the steady-state spectra. The corresponding PL kinetic processes involve two-coupled excited states decaying exponentially with relatively short lifetimes in the sub-nanosecond range. The copolymer presents low crystallinity, high solubility, high thermal stability and high quantum yield. The optical and chemical characterizations of this new copolymer show that it could be a promising candidate as an active component for optical applications in the blue region for light emitting devices and lasers.

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