

Synthesis and Chemical Modification of New Luminescent Substituted Poly(*p*-phenylene) Polymers

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ABSTRACT: A new acyl-functionalized poly(*p*-phenylene) (Ac-PPP) was synthesized by Yamamoto cross-coupling and chemically modified to obtain an anthracene-containing derivative (An-PPP). The chemical structures of the polymers were confirmed by ¹H-NMR, ¹³C-NMR, and FTIR spectroscopic analysis. They are fully soluble in common organic solvents and have number-average molecular weight of 2.70×10^3 and 5.26×10^3 g mol⁻¹ for Ac-PPP and An-PPP, respectively. The optical properties of the polymers were investigated by UV-visible absorption and

photoluminescence spectroscopies. A green emission was observed in Ac-PPP solid thin film and a yellow one in the anthracene-containing polymer An-PPP. The optical bandgap values were 3.21 and 3.08 eV for Ac-PPP and An-PPP, respectively. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: conjugated polymers; poly(*p*-phenylene); Yamamoto cross-coupling; catalyst; photoluminescence; photophysics

INTRODUCTION

Poly(*p*-phenylene) (PPP) and its derivatives are a promising class of organic materials since they combine the excellent thermal and mechanical properties of the rigid aromatic macromolecules to the attractive opto-electronic properties of the semi-conducting polymers.¹ Besides, polyphenylenes are known to display liquid crystallinity² and nonlinear optical properties.³ Moreover, these materials are currently used as active components in several electronic devices, solar cells,⁴ electrode materials for chemical power sources,⁵ and essentially in polymeric light-emitting diodes (PLEDs).^{6–8} They are also exploited in the packaging industry as coating material to protect integrated circuits from breakage, humidity, and corrosion.⁹

However, because of their high crystallinity and insolubility, several approaches have been used to overcome such processability limitations. In this connection, a well used strategy is the introduction of

flexible groups as side chains in the molecular structure of the polymer.^{8,10–14} By this mean not only the polymer solubility was enhanced but also its opto-electronic properties could be modulated and new functionalities could be acquired. Then, the thereby synthesized material can be used for sensing, actuating, and smart materials elaboration.¹⁵

Our work is a contribution in the macromolecular architectural design of PPP derivatives. In previous studies, we have described the electrosynthesis of polyphenylene derivatives from the anodic oxidation of substituted anisole.^{16–18} Unfortunately, the electrochemical technique is not always effective for polymerization because it is tightly depending on the monomer molecular structure. In fact, the introduction of a functionalized side chain on the initial benzenic monomer gave a rise, in some cases, to a change or even the loss of the anodic reactivity of the molecule especially when a withdrawing group was introduced. Alternatively, catalytic coupling reactions have been widely used for this purpose.^{19–}

²¹ In this article, we report the synthesis and the characterization of a new acyl-functionalized PPP (Ac-PPP) prepared by Ni-catalyzed Yamamoto cross-coupling reaction. This polymer was then chemically modified to obtain a PPP derivative containing an anthracene-based pendent group. The optical properties of these two polymers were investigated and compared to evaluate the anthracene introduction effect.

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EXPERIMENTAL

Materials

N,N-dimethylacetamide (DMAc, Aldrich, Steinheim Germany) was dried over calcium hydride (CaH₂) for 2 days under continuous stirring, followed by vacuum distillation and storage over 4-Å molecular sieves under argon atmosphere. Triphenylphosphine (PPh₃, Acros Organics, New Jersey, USA) was recrystallized from hexane (m.p. 78.5–81.5°C). Zinc dust (Zn, Acros Organics, New Jersey, USA) was activated with acetic acid, filtered, washed with dry diethyl ether (Et₂O), and dried under high vacuum at 150°C. 2',5'-Dichloroacetophenone (Aldrich, 98%, Steinheim, Germany), 9-anthracenecarboxaldehyde (Acros Organics, 99 %, New Jersey USA), nickel (II) bromide hydrate (Acros Organics, 98%, New Jersey, USA) and 2,2'-dipyridyl BPY (Acros Organics, 99+%, New Jersey, USA) were used as received.

Measurement and characterization

¹H-NMR and ¹³C-NMR spectral data were obtained on a Bruker AV 300 spectrometer. FTIR spectra were acquired on a Perkin-Elmer BX FTIR system spectrometer by dispersing samples in KBr pellets. UV-visible absorption spectra were recorded on a Cary 5000 UV-vis-NIR spectrophotometer. Photoluminescence (PL) spectra were obtained on a Jobin-Yvon spectrometer HR460 coupled to a nitrogen cooled Si Charged-Coupled Device (CCD) detector. Samples were excited with a 450 W Xenon lamp at 340 nm. For solid-state measurements, the films were spin coated onto a quartz substrate from a 2.10⁻²M chloroform solution. Emissions were detected at 90° from the incident beam with the sample placed at an angle of about 45° to both incident beam and detector.

The solution PL quantum yields were measured in dilute chloroform solution according to a relative method using quinine sulfate (10⁻⁵M solution of 0.5M H₂SO₄) as reference.²² Absorbance of the sample solutions was kept below 0.05 to avoid inner filter effect. Measurements were performed at room temperature using freshly prepared solutions. Both sample and reference solutions were excited at the same wavelength (366 nm) and the PL quantum efficiency of the quinine sulfate solution (ϕ_r) was assumed to be 0.54.²³ Hence, the PL quantum efficiency of the polymer sample (ϕ_s) can be calculated using the following relation: $\phi_s/\phi_r = (A_r/A_s)(F_s/F_r)(n_s^2/n_r^2)$, where, A_r and F_r are absorbance at excitation wavelength and emission integration area for the reference, while A_s and F_s are absorbance and emission integration for the polymer sample. The polymer films for solid-state PL measurement were spin coated onto quartz substrates. Film thickness was controlled by polymer solution concentration

and spinning rate, to obtain comparable thicknesses and so similar refractive indices. Thus, the ratio of PL quantum yields of two film samples can be calculated according to the relation: $\phi_1/\phi_2 = (A_2/A_1)(F_1/F_2)$, where, A_1 and F_1 are absorbance at excitation wavelength and emission integration area for sample 1, while A_2 and F_2 are absorbance and emission integration for the sample 2.

Cyclic voltammetry (CV) was performed on a VoltLab 40 model PGZ 301 in a three-electrode cell containing solution of tetrabutylammonium tetrafluoroborate (*n*-Bu₄NBF₄) 0.1M in acetonitrile. The working electrode was an indium tin oxide (ITO) glass electrode partially covered with a drop-casted polymer films. The voltammetric experiments were performed at room temperature under an argon atmosphere; the scan rate = 50 mV s⁻¹. The potential was measured versus a saturated silver/silver chloride reference electrode (Ag/AgCl). Furthermore, the electrochemical cell was externally calibrated by a ferrocene standard.

Catalyst preparation (NiBr₂BPY)

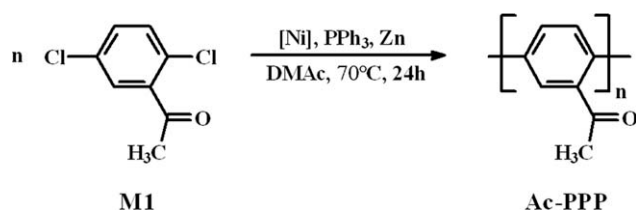
Nickel (II) bromide hydrate (5.50 g, 25.10 mmol) was added to (50 mL) of ethanol in a (250 mL) two neck flask fitted with a reflux condenser. The mixture was heated at 50°C and a solution of 2,2'-dipyridyl (3.15 g, 20.10 mmol) in (25 mL) ethanol was added dropwise via an addition funnel. A green avocado precipitate appears after 13 h. The resulting solid was filtered, washed with ethanol, and dried under high vacuum at 150°C. Yield: 73%.

Modified monomer synthesis (M2)

2',5'-Dichloroacetophenone (2.00 g, 10.00 mmol) and 9-anthracenecarboxaldehyde (2.27 g, 11.00 mmol) were dissolved in (30 mL) of methanol and stirred vigorously. Then, (20 mL) of 2M NaOH aqueous solution (1.60 g, 40.00 mmol) was added dropwise. An orange precipitate appears after 4 h. The resulting solid was filtered, washed with methanol, then precipitated in methanol from chloroform solution. The obtained product was filtered and dried. Yield: 81%. ¹H-NMR (300 MHz, CDCl₃, δ ppm): 8.57 (d, J_{trans} = 16.2 Hz, 1H), 8.45 (s, 1H), 8.23 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.7 Hz, 2H), 7.63 (s, 1H), 7.43–7.63 (m, 6H), 7.1 (d, J_{trans} = 16.2 Hz, 1H). ¹³C-NMR (75 MHz, CDCl₃, δ ppm): 191.8, 144.2–125.0. m.p.: 153°C.

Synthesis of the acylated PPP (Ac-PPP)

2',5'-Dichloroacetophenone (2.00 g, 10.00 mmol), Zn powder (2.00 g, 30,60 mmol), NiBr₂BPY (0.38 g, 1.00 mmol), and PPh₃ (1.04 g, 4.00 mmol) were added into a (100 mL) long-neck flask with a side tubing



Scheme 1 Synthetic route to Ac-PPP.

capped by a rubber septum and a reflux condenser. The system is connected to an argon bubbler and set in an oil bath. While heating and stirring magnetically, 15 mL of DMAc was added by syringe through the septum. When temperature reached to 35°C a brown color formed at 50–60°C, the color became deep red-brown. At 70°C the solution became dark brown and after 24 h this color disappeared to leave a grey Zn suspension. The mixture was then diluted with chloroform filtered to remove Zn, concentrated and precipitated twice in methanol. The resulting yellowish fine powder was filtered, washed with methanol and dried under high vacuum. Yield: 60%.

$^1\text{H-NMR}$ (300 MHz, CD_2Cl_2 , δ ppm): 8.40–6.70 (aromatic CH), 2.80–2.00 (CH_3CO). $^{13}\text{C-NMR}$ (75 MHz, CD_2Cl_2 , δ ppm): 203.5 (C=O), 141.4–127.5 (aromatic C), 31.2, 25.3 (2 CH_3).

Synthesis of the substituted PPP derivative (An-PPP)

Ac-PPP (0.27 g, 2.30 mmol) and 9-anthracenecarboxaldehyde (0.71 g, 3.45 mmol) were dissolved in 30 mL of tetrahydrofuran and stirred vigorously. Then, 20 mL of 0.5M NaOH aqueous solution (0.24 g, 10 mmol) was added dropwise. After 48 h, the mixture was acidified by adding 1M HCl aqueous solution. The polymer was extracted with chloroform, washed with water, dried over MgSO_4 , concentrated and then precipitated first time in methanol and second time in diethyl ether. An orange fine powder was obtained.

$^1\text{H-NMR}$ (300 MHz, CD_2Cl_2 , δ ppm): 8.72–6.24 (aromatic and vinylic CH), 2.59–2.19 (CH_3CO). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , δ ppm): 196.8 (C=O), 140.4–126.1 (aromatic and vinylic C), 25.3 (CH_3).

RESULTS AND DISCUSSIONS

Synthesis of the acylated PPP (Ac-PPP)

Ac-PPP was synthesized by the Ni-catalyzed Yamamoto cross-coupling reaction. In fact, this polycondensation is one of the most used routes to PPPs.^{17,18} Originally developed for synthesis of biphenyls,²⁴ it consists in Ni(0) coupling procedure of bis(aryl halide) monomers. This procedure, with

minor modifications, is reported to yield high molar mass PPPs with good conversions.²⁵ However, the catalyst system is sensitive to sources of hydrogen in the reaction mixture and also to monomers containing functionality may adversely coordinate with Ni(0) and lead to their reduced form. Ac-PPP was prepared by Ni(0) catalytic coupling of 2',5'-dichloroacetophenone in DMAc with 60% yield (Scheme 1).

The used catalyst was prepared *ex situ* according to a previously described procedure.^{26,27} The relatively moderate yield of the polycondensation can be explained by the fact that a part of the monomer is reduced to acetophenone. This is due to the presence of proton sources like water traces in the solvent, which are responsible for the formation of hydride complex by halide–hydrogen displacement.²⁵ Other work refers also to secondary reactions including the transfer of aryl groups from the PPh_3 ligand.^{25,28}

The polymer was found to have good solubility in common organic solvents such as tetrahydrofuran, chloroform, methylene chloride, dimethylformamide, and dimethylacetamide. The structure was confirmed by NMR and FTIR spectroscopic analysis. The $^1\text{H-NMR}$ spectrum (Fig. 1) showed a broad peak between 8.40 and 6.70 ppm assigned to phenylene protons. The CH_3CO group appears in the ranges 2.80–2.00 ppm. The $^{13}\text{C-NMR}$ spectrum (Fig. 2) showed a peak at 203.5 ppm assigned to the carbonyl group. The aromatics carbons appear between 127.5 and 141.4 ppm. The methylene groups appear at 31.2 ppm; however, those corresponding to the end chain carbons appear at 25.3 ppm.

The FTIR spectrum (Fig. 3) showed absorption band due to aromatic C–H stretching at 3056 cm^{-1} . The valence bands of the aliphatic C–H groups are seen between 3000 and 2852 cm^{-1} . The carbonyl group appears at 1689 cm^{-1} . The aromatic ring C=C stretching vibrations appear between 1469 and 1431 cm^{-1} . The out-of-plane vibration of the aromatic hydrogens shows a strong absorption at 822 cm^{-1} .

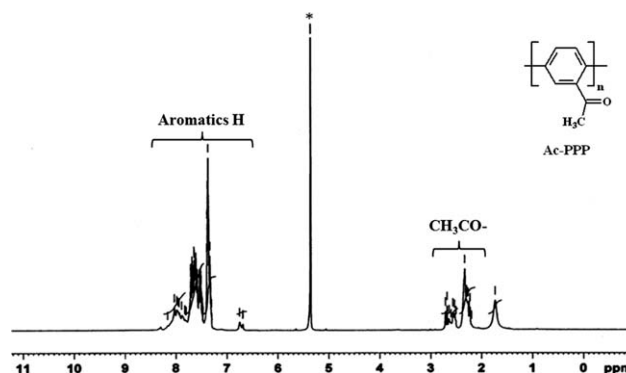


Figure 1 $^1\text{H-NMR}$ spectrum of Ac-PPP, (*: methylene chloride).

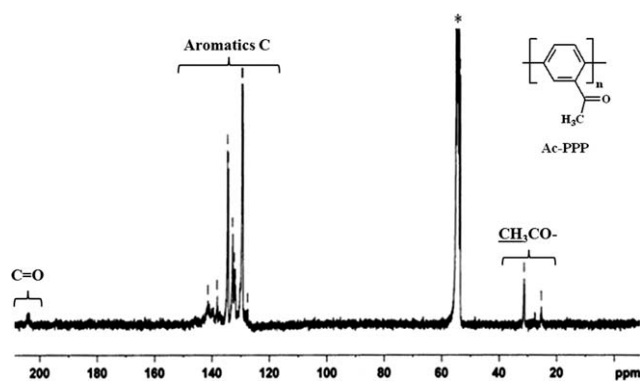


Figure 2 ^{13}C -NMR spectrum of Ac-PPP (*: methylene chloride).

By Gel Permeation Chromatography (GPC) analysis, the polymer number-average molar weight was determined to be 2.70×10^3 g/mol and the polydispersity index (Ip) was of 2.

Bloom et al. reported that a partial reduction of carbonyl groups to secondary alcohols can take place during the polymerization of the dichlorobenzophenone derived monomer to corresponding poly(benzophenone).^{29,30} Such side reaction would be an obstacle for the modification of Ac-PPP in Claisen condensation step. However, the ^{13}C NMR (Fig. 2) and the FTIR (Fig. 3) spectra reveal the complete absence of secondary alcohol function in the polymer (^{13}C NMR: C—OH: 65–80 ppm; FTIR: O—H stretching at 3500 cm^{-1}).

Preparation of the substituted PPP derivative (An-PPP)

Incorporation of the anthracene-based side-groups on the Ac-PPP was realized via the simple and easy Claisen condensation,³¹ using the 9-anthracenecarboxaldehyde (Scheme 2).

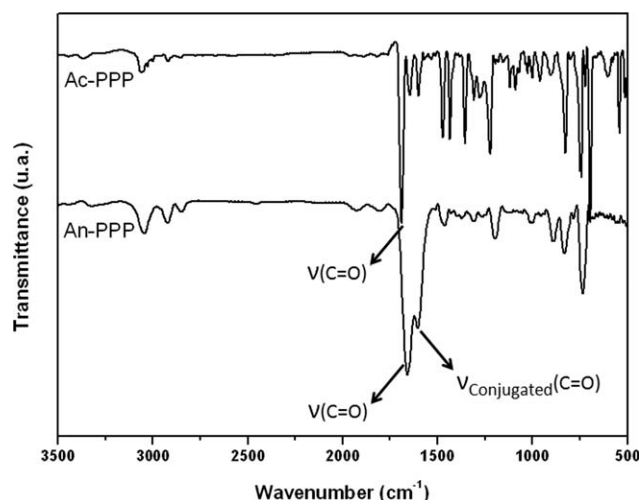
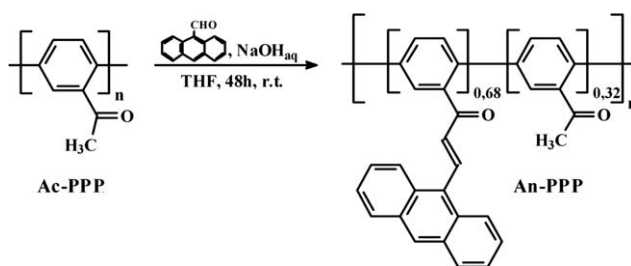


Figure 3 FTIR spectra of Ac-PPP and An-PPP.



Scheme 2 Synthetic route to An-PPP.

Such reaction is generally monitored in alcohol; however, we chose THF as solvent in order to solubilize the Ac-PPP as well as the modified polymer, and to obtain a high degree of modification. An excess of aldehyde (1.5 equiv.) was used to drive the modification reaction and it was removed during the purification stage. The polymer modification was confirmed by NMR and FTIR analysis. Indeed, Figure 4 shows the decrease of relative intensity of acyl protons peak and the appearance of the vinyl ones starting from 6.24 ppm. The substitution ratio can be determined using ^1H -NMR data by comparing the integrations of acyl protons peak and the aromatic/vinyl protons one. A value of 67% was calculated and demonstrates only a partial modification of Ac-PPP, probably caused by the steric hindrance of the bulky anthracene moiety. The FTIR spectrum (Fig. 3) showed two absorption bands due to carbonyl groups stretching. The non-conjugated C=O appears at 1660 cm^{-1} while the conjugated one appears at 1604 cm^{-1} .

Based on the Ac-PPP weight, the molar mass of the substituted An-PPP was calculated to be 5.61×10^3 g/mol. The GPC-determined number-average molar weight was in fact close to this value (Table I).

On the other hand, it is worthy to note that we could have carried out a direct polycondensation of the anthracene-substituted monomer (M2). Indeed, this strategy can lead to a totally substituted polymer chain with a well-defined structure. However,

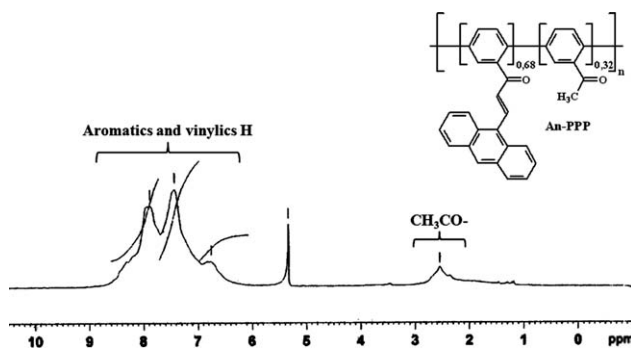


Figure 4 ^1H -NMR spectrum of An-PPP (*: methylene chloride).

TABLE I
Molar Weight of the Polymers

Polymer	Substitution ratio (%) (¹ H-NMR)	M_n -NMR (10^3 g/mol)	M_n -GPC (10^3 g/mol)	I_p
Ac-PPP	–	–	2.70	2.0
An-PPP	67	5.61	5.26	2.1

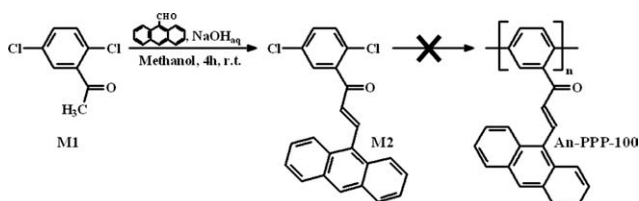
using such a procedure presents, generally, some complications related to side reactions which can occur between the catalytic system and some reactive pendant-groups. Furthermore, it is necessary to assess the pendant-group electronic and steric effects on the ability of the monomer to polymerize.

Consequently, we have tested the direct polycondensation of the modified monomer (M2) via the Yamamoto reaction (Scheme 3). Nevertheless, the desired polymer was not obtained. In order to elucidate the reason of this failure, a dehalogenated-M2 monomer, obtained by reaction between acetophenone and 9-anthracenecarboxaldehyde, was subjected to the same polymerization conditions. We noticed the same changes of color in the reaction medium. An orange powder was isolated and cannot be characterized by NMR. This evidenced the nickel–vinyl interaction making competition with the coupling reaction of dihaloaromatic moiety.^{32–34}

Optical properties

The UV–visible absorption and fluorescence spectra of Ac-PPP and An-PPP, in solid thin film and in chloroform dilute solution, are shown in Figures 5 and 6. Table II summarizes the polymers optical characteristics. In solution, Ac-PPP absorbs at 320 nm, whereas An-PPP shows a maximum at 336 nm. The absorption onset values were 370 and 486 nm for Ac-PPP and An-PPP, respectively. Thus, An-PPP exhibits a more important effective conjugation length which can be related to an eventual improvement of PPP backbone planarity via introduction of the bulky vinylanthracene groups or/and the incorporation of such conjugated side-chain within the polymer conjugated system.

Besides, Ac-PPP presents a blue emission with a maximum at 455 nm whereas An-PPP showed a red-shifted emission with a maximum at 555 nm (yellow). Thus we notice the possibility of modula-



Scheme 3 Direct pathway for 100% substituted An-PPP.

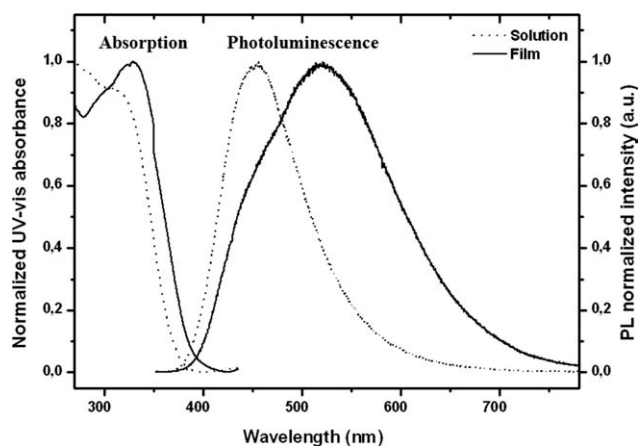


Figure 5 UV-visible absorption and PL spectra of Ac-PPP.

tion of the photophysical behavior of PPPs by the incorporation of the vinyl anthracene side-group.

In the film state, Ac-PPP presents an absorption maximum at 329 nm whereas we observed only a shoulder at about 330 nm for An-PPP (Figs. 5 and 6). The optical band gaps were estimated from the absorption onset of the polymers films. The calculated values were 3.21 and 3.08 eV for Ac-PPP and An-PPP, respectively. In comparison with the dilute solution, the UV–visible spectrum of the Ac-PPP film was broader and the absorption onset was red-shifted. Such behavior is in fact generally observed in π -conjugated polymers and was attributed to the π - π stacking of conjugated segments and interchain interactions in the solid state.³⁵ In the case of An-PPP film, we noted in return a slightly blue-shifted spectrum in comparison with the solution. These results suggest weaker π - π interactions in An-PPP film. The restriction of PPP units stacking is probably due to the steric repulsion of the bulky anthracene groups. The π - π stacking of conjugated moieties also influences the film emission and a broad

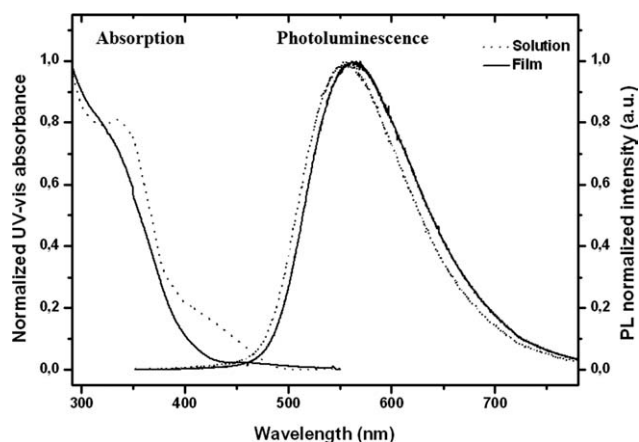


Figure 6 UV–visible absorption and PL spectra of An-PPP.

TABLE II
Optical Data of Ac-PPP and An-PPP

	Absorption			Photoluminescence		
	λ_{\max} (nm)	ϵ_{\max} ($10^4 M^{-1} \text{ cm}^{-1}$)	λ_{onset} (nm)	λ_{\max} (nm)	FWHM ^a (nm)	Stokes Shift (nm)
Dilute solution in chloroform						
Ac-PPP	320	0.38	370	455	94	135
An-PPP	336	0.73	486	555	119	219
Thin film						
Ac-PPP	329	11.17	386	520	171	191
An-PPP	330 ^b	9.48	402	562	124	232

^a Spectrum full width half maximum.

^b Shoulder.

red-shifted PL spectrum was obtained in Ac-PPP as consequence of excimer formation.³⁶ Minor red-shift and broadening values were observed for An-PPP upon going from solution to film.

The fluorescence quantum efficiencies of the polymers were determined in dilute chloroform solution by a relative method using quinine sulfate as standard. A value of 0.23 was obtained for Ac-PPP; in the case of An-PPP the quantum yield of fluorescence decreases to 0.09 ($\phi_{\text{An-PPP}}/\phi_{\text{Ac-PPP}} = 0.4$). This behavior is probably related to a reduction in the rigidity of the structure by the introduction of vinylanthracene side groups. In the case of conjugated polymer films, a luminescence loss via the quenching processes caused by π -stacking was generally observed, and the obtained PL quantum yield was lower than that of solution.³⁷ In solid thin films, the ratio of PL quantum yields of An-PPP and Ac-PPP ($\phi_{\text{An-PPP}}/\phi_{\text{Ac-PPP}}$) was about 0.64, which is significantly greater than that of solutions. Indeed, in comparison with Ac-PPP, the An-PPP presents weaker π - π interaction and consequently less loss of PL while passing from the solution to film.

Electrochemical properties

To investigate the redox behavior of Ac-PPP and An-PPP and to estimate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, cyclic voltammetry (CV) was applied to the polymer films. In fact, the knowledge of the HOMO and LUMO energy levels is of crucial importance to the selection of cathode and anode materials for PLED devices.³⁸ The use of CV analysis is of good reliability as the electrochemical processes are similar to those involved in charge injection and transport processes in PLEDs.³⁹ The polymers were drop-coated onto ITO glass substrate and scanned both positively and negatively in (*n*-Bu₄NBF₄)/acetonitrile solution. The onset of oxidation ($V_{\text{onset-ox}}$) was located at 1.33 V for Ac-PPP and at 0.94 V for An-PPP (vs. Ag/AgCl).

According to an empirical method^{40–42} and by assuming that the energy level of the ferrocene/ferrocenium is 4.8 V below the vacuum level, the HOMO energy level can be calculated as follow:

$$E_{\text{HOMO}}(\text{IP, ionisation potential}) = -(V_{\text{onset-ox}} - V_{\text{FOC}} + 4.8)\text{eV}$$

where V_{FOC} is 0.71 V, the ferrocene half-wave potential measured versus Ag/AgCl.

Thus, E_{HOMO} values of Ac-PPP and An-PPP were estimated to be -5.42 and -5.03 eV, respectively. The results suggest an improved hole-injection ability of An-PPP, which agree with the increase of effective conjugation length due to the incorporation of high electron-density vinyl anthracene groups.

On sweeping the polymers cathodically, no clear reduction peaks were observed. Based on the bandgap obtained from the optical method and HOMO level values,^{43,44} the LUMO levels were calculated to be -2.21 and -1.93 eV for Ac-PPP and An-PPP, respectively.

CONCLUSION

A new acylated PPP derivative (Ac-PPP) was synthesized via the Ni-catalyzed Yamamoto coupling. This polymer was then partially modified by Claisen condensation to elaborate a PPP copolymer containing anthracene-based side groups (An-PPP). The structures of the polymers were confirmed by spectral methods and a 67% substitution ratio was estimated. The optical properties of the An-PPP and Ac-PPP were investigated and compared, in dilute solutions and as thin films. An emission centered at 455 nm was observed for Ac-PPP solution; and a 100 nm red-shifted PL spectrum was observed for An-PPP. The Ac-PPP film characterization showed an important π - π stacking interaction between conjugated PPP segments. In return, very weak interaction was observed in An-PPP film, due to the presence of stacking-preventing anthracene groups.

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