

Synthesis of substituted conjugated polymers: Tuning properties by functionalization*

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Abstract: The review addresses features of special interest concerning two classes of functionalized semiconducting polymers: poly(aryleneethynylene)s (PAEs) bearing biomolecules as chiral nonracemic pendant groups and poly(phenylenevinylene)s (PPVs), which are fluorinated in various positions of the repeating units. Molecular design and choice of specific substituents, synthetic protocols, and the effect of functionalization on properties of the polymers both in solution and in the solid state are discussed.

Keywords: conjugated polymers; organic synthesis; organic semiconductors; cross-coupling reactions; chiral polymers; fluorinated polymers.

INTRODUCTION

π -Conjugated polymers represent a very promising class of organic materials for photonics and electronics, which exhibits a unique combination of optical and electrical properties typical of semiconductors with processing advantages and mechanical features of polymers [1]. Remarkable academic and industrial research efforts have been made over the last few decades, and are nowadays still vigorous, in view of the use of these materials in a variety of thin and flexible “plastic” optical and electronic devices such as organic light-emitting diodes (OLEDs), organic field effect transistors (OTFTs), organic solar cells, and electrical and optical sensors. A key advantage of organic electronic devices in large-scale production is represented by the low-cost processing that is based, in most cases, on solution deposition methods and has been extended to ink-jet printing technology. Recently, displays based on OLEDs have been commercialized, and very attractive market shares are foreseen also for other applications of organic semiconductors.

Indeed, the most peculiar characteristic of organic semiconductors, when compared with the inorganic counterparts, is represented by their wide structural variety which offers a powerful tool for the control of properties by molecular design guided by the understanding of structure–property relationships. A first level of molecular control of the properties is represented by the choice of the conjugated backbone, i.e., the structure and the sequence of the conjugative units (double and triple bonds, aromatic rings). The basic structures of some of the most common π -conjugated polymers are reported in Fig. 1.

Functionalization of the conjugated skeleton represents a further level of structural modulation of properties. Steric and electronic effects of substituents can finely tune properties of organic semi-

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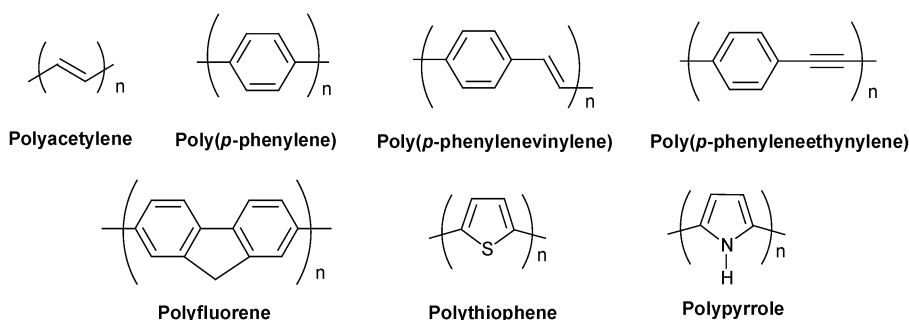


Fig. 1 Chemical structures of some conjugated polymers.

conductors not only at the single-molecule level, by modifying electronic distribution and effective conjugation of the π -system, but also in the solid state by modulating intermolecular interactions. Supramolecular organization strongly affects the optical and electrical behavior of the materials. Therefore, control of interchain interactions by chemical functionalization and appropriate choice of the deposition techniques, aimed to optimize material performances in devices, is a very important research subject [2]. Moreover, substituents on the main chain can be introduced to confer selective recognition properties when the organic semiconductor has to be used as the active layer in optical or electrical sensor devices.

Fast evolution of the field demands increasingly complex molecular structures, which must also be characterized by a high level of purity, structural regularity, and absence of chemical defects. Therefore, it is evident that development of efficient and selective synthetic methodologies plays a key role in the progress of this research area.

In the last decade, we have contributed [3] several synthetic protocols, mainly based on organometallic reactions, for conjugated oligomers and polymers, including poly(arylenevinylene)s, (PAVs), poly(aryleneethynylene)s (PAEs), and polyarylenes.

Herein, we report an overview of our more recent results focusing on two classes of functionalized conjugated polymers: (i) PAEs bearing chiral biomolecules as substituents and (ii) fluorinated poly(phenylenevinylene)s (PPVs). The synthetic challenges will be discussed together with features conferred by the special functionalizations and some applications of the two classes of polymers.

POLY(ARYLENEETHYNYLENE)S FUNCTIONALIZED WITH CHIRAL BIOMOLECULES

PAEs represent one of the most intensively investigated classes of conjugated polymers because their optical and electrical properties are attractive for a wide variety of applications. In fact, PAEs are fluorescent both in solution and in the solid state and they generally show enhanced photostability in air in comparison with other common classes of luminescent polymers, such as PAVs. The PAEs also exhibit chromogenic behavior, including solvatochromicity, thermochromicity, ionochromicity, and surfactochromicity [4].

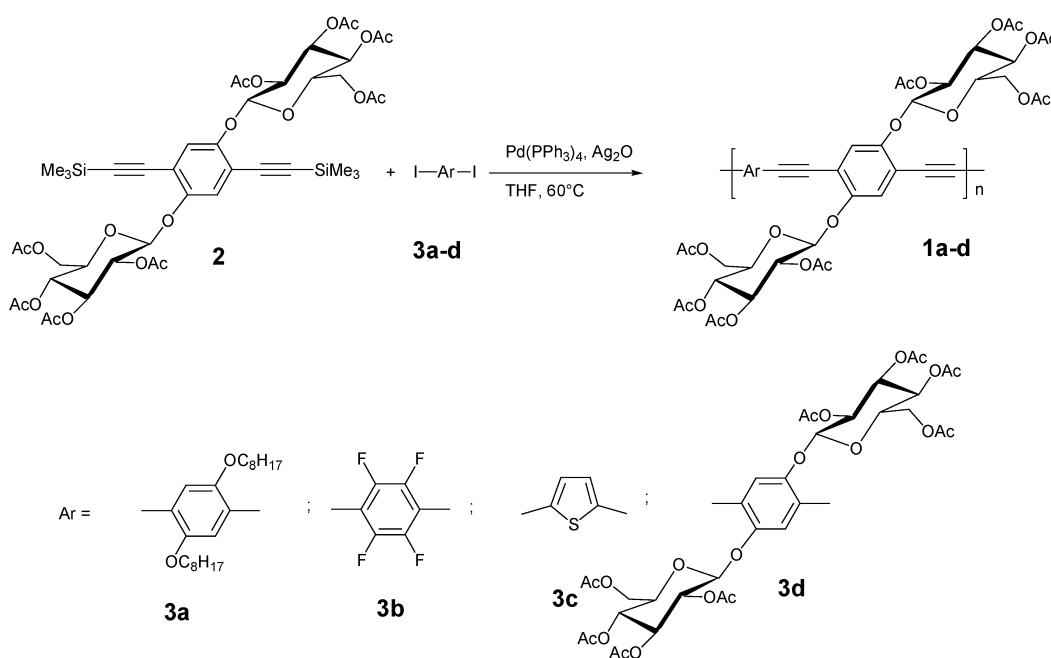
OLEDs [5], molecular wires [6], and polarizers for liquid-crystal (LC) displays [7] have been fabricated using PAEs as active materials. Moreover, PAEs are an important class of semiconducting polymers for chemo- and biosensing applications, especially those based on colorimetric and fluorescence detection methods [8].

An impressive number of structural modifications have been developed to adjust properties for specific applications, greatly expanding the PAEs' family. In particular, substituents attached to the conjugated PAE skeleton can modulate electronic and optical properties, but also confer solubility in specific solvents, self-aggregation, and/or molecular recognition ability.

Among the wealth of possible groups that can be bonded to the conjugated main chain, special interest is attached to functionalization with biomolecules that can result in semiconducting or highly fluorescent active materials for chemo- and biosensing applications. Moreover, some classes of biological molecules represent easily available sources of enantiopure compounds, so they can be used as chiral nonracemic substituents for the conjugated backbone, with many interesting consequences. First, chiral substitution enables the use of chiro-optical techniques for structural investigation on the polymers both in solution and in the solid state; second, multifunctional chiral molecules can be used as chiral selectors in enantioselective organic semiconductor-based sensors. Finally, polarized light emission can be obtained by chiral-substituted π -conjugated polymers properly arranged in the solid state.

Two basic synthetic approaches to biofunctionalized PAEs can be envisaged. According to the most common strategy, introduction of biosubstituents is performed after the synthesis of the polymers, which bear reactive side groups able to bind the biomolecules. The strategy is general and straightforward but, in most cases, it offers poor structural control on the number and positions of substituents actually linked to the main chain. The alternative strategy, which has been less commonly investigated, is based on polymerization of monomers previously functionalized with biomolecules. Such an approach, which can be used with small biomolecules, is to be preferred when the polymer is synthesized for applications requiring high levels of structural regularity or a high number of bioreceptors bonded to the conjugated backbone.

We followed the latter approach for the synthesis of PAEs bearing peracetylated D-glucose molecules as substituents **1a–d** (Scheme 1) [9]. The polymerization process consisted in cross-coupling reaction between the bis(trimethylsilylethynyl) derivative **2**, bearing two protected D-glucose molecules bonded to the aromatic ring by a β -glucosidic linkage, and the diiodo arenes **3a–d**, under Pd catalysis and in the presence of silver oxide. This methodology was preferred to the classic Cassar–Heck–Sonogashira cross-coupling process commonly used in PAE synthesis, since it was demonstrated to produce a lower amount of defects deriving from oxidative homocoupling reaction of the ethynyl derivative, and it had been applied to the synthesis of different PAEs with a simpler struc-



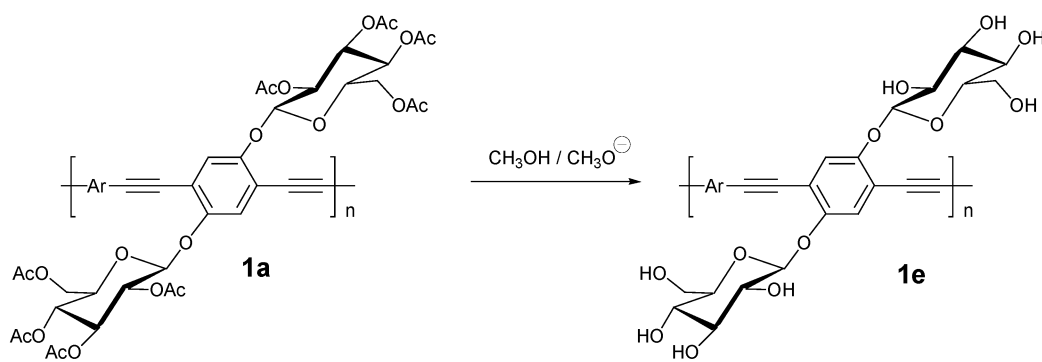
Scheme 1

ture [10]. Actually, in our case, NMR spectroscopy showed the absence of structural defects that could derive from oxidative homocoupling of the monomer **2**.

The three PAE copolymers **1a–c** obtained are characterized by regular alternation of aromatic rings substituted with two glucose molecules, and alkoxy- or tetrafluorosubstituted phenylene or thiophene rings. The glucose units can also be present in both the bis(silylethynyl) derivative **2** and the iodoaromatic monomer **3d**, thus affording the polymer **1d** whose aromatic rings are all substituted with two glucose units.

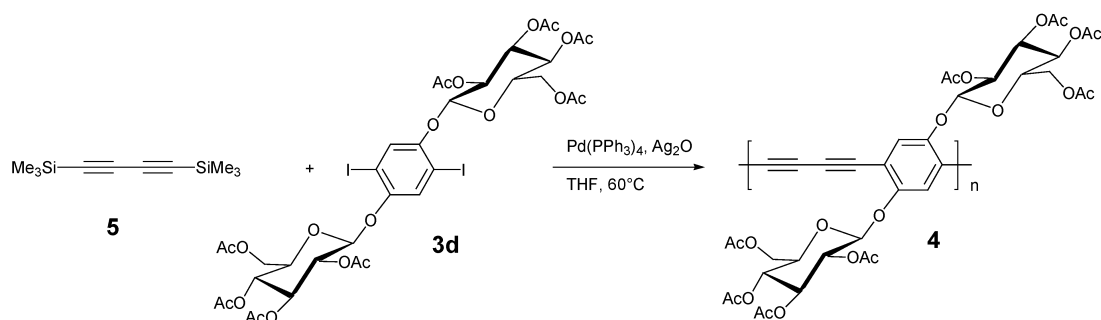
Similar PAEs were also prepared using the standard Cassar–Heck–Sonogashira coupling between a penta-*O*-acetylglucose functionalized aromatic dihalide with a 2,5-dialkyl-1,4-bis(ethynyl)benzene by the Bunz group [11].

The hydrolysis of **1a** (Scheme 2), easily conducted by an alkali (MeO-/MeOH) treatment, led to the corresponding deacetylated polymer **1e**, soluble in polar solvents (methanol, dimethylsulfoxide) and moderately soluble in water [9].



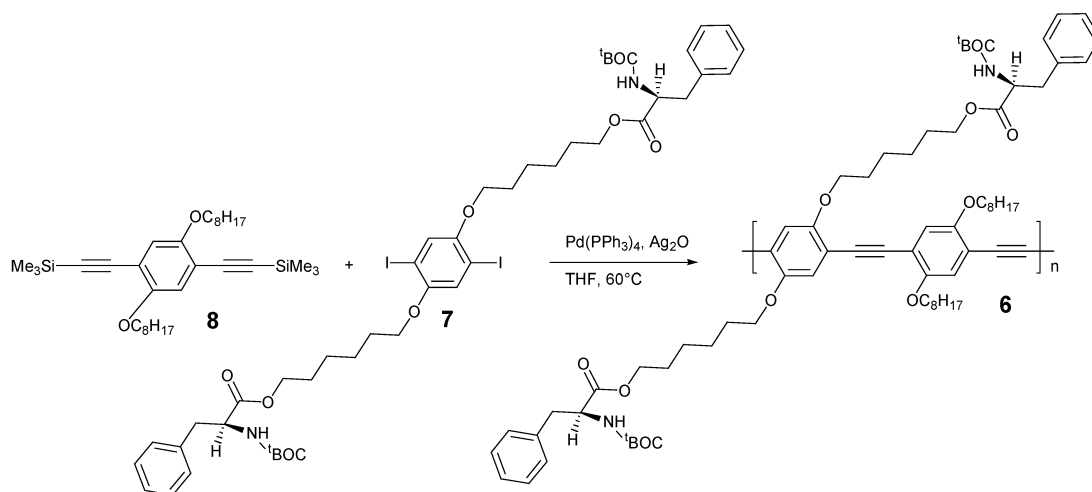
Scheme 2

A similar polymerization protocol could also be used for the synthesis of polymer **4** containing butadienylene units, employing the butadiyne **5** and the aromatic derivative **3d** according to Scheme 3.



Scheme 3

The synthesis of PAE **6** functionalized with *t*-BOC protected L-phenylalanine units was carried out using the same polymerization reaction (Scheme 4) [12]. In this case, the biomolecule is introduced on the aromatic halide partner **7** that is reacted with the bis-(trimethylsilylethynyl) alkoxy substituted aromatic derivative **8**. In polymer **6**, the amino acid substituent is not directly bonded to the aromatic



Scheme 4

ring, as in the case of the glucose substituent, but it is connected through a six carbon atom alkoxy spacer that is linked to the phenylalanine carboxylic group through an ester bond.

Poly(phenyleneethynylene)s (PPEs) are well known for their tendency to form aggregates and excimers in various solvents or solvent mixtures (defined solvent nonsolvent mixtures) [13], with strong consequences on optical properties (solvatochromism, reduction of luminescence efficiencies). Formation of aggregates was detected by absorption and luminescence spectroscopies for both the glucose-substituted **1a** and the amino acid-functionalized **6** polymers in methanol/chloroform and ethanol or hexane/chloroform mixtures, respectively. On the contrary, no aggregate formation could be detected in the case of the PPE **1e** bearing nonprotected glucose units (**1e** is insoluble in chloroform that, in the present case, is used as the nonsolvent component). This represents an example of how substituents can affect not only solubility, but also intermolecular interactions and, in turn, aggregation and solid-state behavior. The presence of enantiopure L-phenylalanine units in side chains of **6** allowed us to use chiroptical techniques (circular dichroism and circularly polarized luminescence) to gain a deeper understanding of structure and nature of the elicited aggregates, which are effectively generated with the aid also of strong intermolecular interactions of polar protected amino acid units. The whole set of spectroscopic data has led us to conclude that the presence of chiral side chain prevents PPE **6** from forming linear supramolecular aggregates, leading to supramolecular chiral packing of the polymer chains in the aggregates. Furthermore, the similarity of the (chiro)optical properties of the supramolecular aggregates with those recorded in thin film of the same polymer **6** cast from chloroform solution permitted extension of the proposed structural organization as well as the considerations on the nature of interchain interactions in the aggregates to those existing in solid phase. As an interesting consequence of the chiral supramolecular organization induced by the amino acid side groups, the fluorescence is only reduced and not completely quenched in aggregates and thin films. Furthermore, circularly polarized luminescence has been recorded in thin films of **6** that may find application in novel polarized light-emitting optoelectronic devices [12]. These observations demonstrate how a proper choice of the chiral pendants can be exploited to modulate markedly supramolecular interactions, with the aim to tune material properties.

Both the protected D-glucose and L-phenylalanine substituents are chiral multifunctional molecules, thus they can enantioselectively interact with chiral compounds and, consequently, can confer chiral recognition properties to the PPEs in sensor devices. Chiral discrimination ability of both polymers **1a** and **6** toward menthol enantiomers, used as test chiral vapor analytes, was demonstrated using the polymers as active layers in quartz crystal microbalance gravimetric sensors [14]. In such piezo-

electric devices, a quartz crystal covered by a thin film of the active material undergoes changes in vibration frequency related to mass variations that, in turn, are dependent on the amount of the analyte that is chemi-adsorbed on the active layer. The difference in the response of the glucose-substituted polymer **1a** to the two menthol enantiomers was measured to be 10 %, with the polymer interacting more favorably with the natural (–) menthol. Response difference rises up to 28 % in the case of the amino acid-substituted polymer **6** used as the active layer, with inverted selectivity that, in this case, is more favorable to the (+) enantiomer[15].

FLUORINATED POLY(PHENYLENEVINYLENE)S

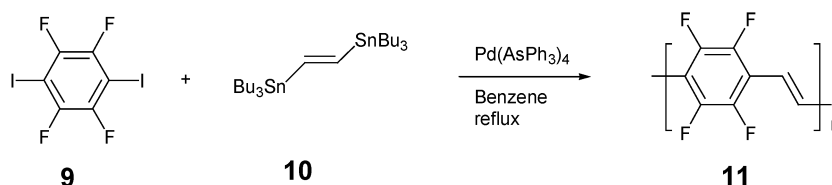
Since its use as emitting material in the first organic polymer-based light-emitting diode by Friend and coworkers [16], poly(*p*-phenylenevinylene) and an impressive number of its derivatives obtained by a variety of synthetic methodologies have been subjected to continuous investigation as active materials not only for OLED devices, but also for other applications of organic semiconductors such as optically pumped lasers and photovoltaic systems [17].

PPVs can be prepared by the “precursor routes” (Gilch [18] or Wessling [19]), which are based on the synthesis of soluble nonconjugated polymers that are subsequently subjected to an elimination process, thus affording the final conjugated materials. These methodologies are versatile and can be scaled up to a large-quantity production. Other classical processes for carbon–carbon double bond formation, such as the Wittig reaction [20] and the Knoevenagel condensation [21], have been adopted as polymerization reactions leading to PPV polymers. Organometallic methodologies, conveniently used for regio- and stereoselective synthesis of 1,2-disubstituted olefins, appeared soon as suitable synthetic tools for preparation of PPVs, especially when a high degree of structural stereo- and regio-regularity was required. Accordingly, many of the classical Pd-catalyzed coupling reactions (Heck, Suzuki–Miyaura, Stille) involving vinylic reagents have been exploited to obtain PPVs bearing substituents in various positions, more frequently on the aromatic rings [3]. In particular, we have widely exploited the Stille cross-coupling reaction of bis(stannyl)ethylene with variously functionalized aromatic bis-iodides, as a versatile and general synthetic methodology yielding PPV polymers characterized by high stereoregularity and absence of conjugation defects [22].

Functionalization of the PPV backbone with fluorine atoms or fluorinated substituents can confer attractive features to the resulting materials due to the high electronegativity of the fluorine atom and to the strength of the fluorine–carbon bond [23]. Replacement of carbon–hydrogen bonds by stronger and less reactive carbon–fluorine bonds has been proposed as a possible approach for increasing the chemical stability of PPVs against photooxidation, with consequent improvement of the lifetime of these semiconducting polymers, a feature that would greatly increase their role in commercial devices. Moreover, theoretical calculations have shown that the introduction of electron-withdrawing substituents onto either the arylene rings or the vinylene units of PPV can lower the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the polymer [24], and this would represent an important step toward improvement of PPV-based OLED efficiencies and simplification of the device architecture. In fact, an issue still associated with the use of PPV polymers in electroluminescent devices is represented by their poor electron-accepting character, due to high LUMO level so that, in order to achieve efficient emission, low work function metal cathodes, generally calcium, and adjunctive electron-transporting layers between the cathode and the emitting film must be used. On the other hand, a sufficiently low LUMO energy level would permit us to use more stable higher work function metal cathodes, such as aluminum, and to avoid additional electron-transporting materials. Lowered HOMO levels would also result in increased oxidation potential and enhanced stability against photooxidation. Changes in optical properties, and, in particular, blue-shifted emission and absorption, are also expected as a consequence of the functionalization with fluorine atoms. In this respect, it is worth noting that the investigation on efficient blue-emitting semiconducting polymers for display applications is still an open research field. As a consequence, blue emission

from fluorinated PPVs would represent a relevant achievement. Finally, fluorination of the conjugated backbone can strongly affect interchain interactions and supramolecular aggregation in the solid state due to inverted charge density distribution in fluorinated aromatic compounds and to F...H-C interactions.

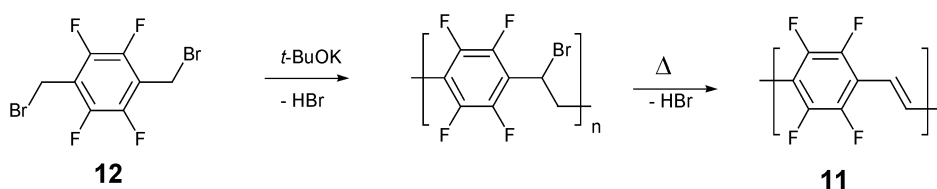
All these intriguing features prompted us to extend to fluorinated PPV polymers our synthetic organometallic routes to PPVs based on the Pd-catalyzed coupling of vinyl stannanes with aromatic halides (Stille reaction) [3,22]. In fact, Pd-catalyzed Stille cross-coupling polymerization of 1,4-diiodotetrafluoro benzene **9** with (*trans*)-1,2-bis(tributylstannyl)ethylene **10** afforded poly(2,3,5,6-tetrafluoro-1,4-phenylenevinylene) (PTFPV) **11** (Scheme 5) [25], whose synthesis had been previously unsuccessfully attempted both via water- and organic solvent-soluble precursor routes [26].



Scheme 5

The product **11**, although insoluble in common organic solvents, was fully characterized by matrix-assisted laser desorption ionization with time-of-flight (MALDI-TOF) mass spectrometry while IR spectroscopy allowed the assignment of the *trans* configuration to the vinylene units. A thin film of the polymer, obtained by thermal evaporation under high vacuum, was used as emitting layer in an OLED device fabricated using indium tin oxide (ITO) as the anode and aluminum as the cathode metals. Introduction of a hole-transporting [*N,N*-9-bis(3-methylphenyl)-*N,N*-9-diphenylbenzidine] (TPD) layer between the ITO anode and the emitting PPV polymer **11** was necessary to obtain emission of green light with a threshold voltage of 6.5 V. The need of the TPD layer indicates a high energy barrier for the hole injection from the anode, while a lower energy barrier should occur between the Al cathode and the conduction band of the fluorinated PPV emitter, as a result of the increased electron affinity of the polymer caused by the presence of the fluorine atoms.

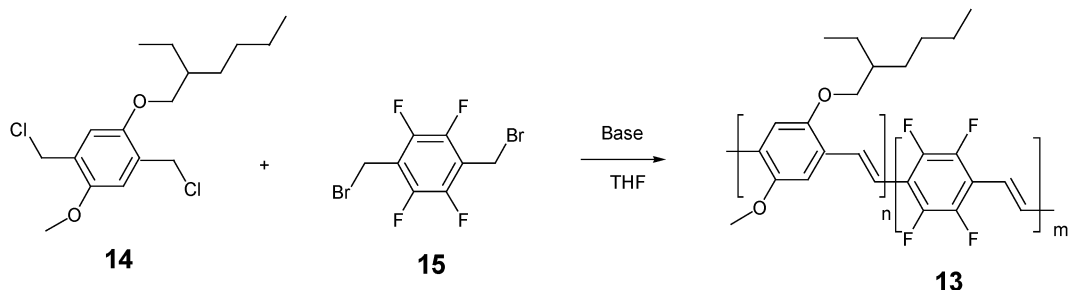
Later, the synthesis of PTFPV **11** by a modified soluble precursor route starting from the brominated monomer **12** (bromine precursor route, BPR) was reported by Gan et al. (Scheme 6) [27] but the polymer obtained was not as structurally ordered as the one prepared via the organometallic approach described above. Indeed, the presence of *cis* double bonds was spectroscopically detected in the polymer, and the possible presence of trace amounts of unconverted precursor units may be responsible of the multi-peak characteristics observed in the photoluminescence spectrum.



Scheme 6

The simultaneous functionalization of the PPV polyconjugated backbone with electron-withdrawing fluorine atoms and electron-donating groups, such as alkoxy substituents, appears of interest as a structural modification that may confer intriguing optical and electronic properties. Indeed, it was

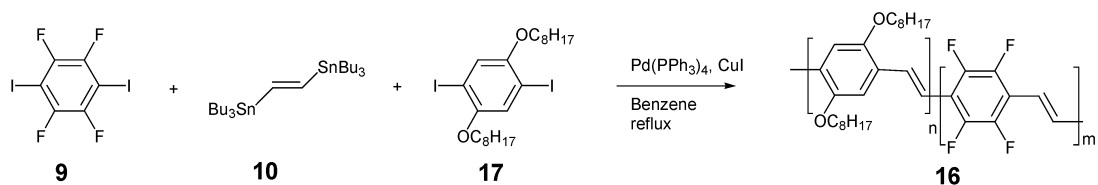
demonstrated that introduction of alkoxy and cyano groups on PPV skeleton is a valuable strategy to adjust the HOMO and LUMO levels to match the work functions of the anode and cathode metal electrodes, respectively, used in OLED devices, thus improving efficiencies [28]. In 2000, Caciali and coworkers [29] reported the synthesis of random copolymers **13** of fluorine- and alkoxy-substituted poly(*p*-phenylenevinylene)s by the Gilch-type polymerization of bis(halomethyl) benzenes **14** and **15** in tetrahydrofuran (THF) (Scheme 7).



Scheme 7

Varying the comonomer feed ratios, it was possible to obtain copolymers incorporating fluorinated units in weight percentages of 7, 14, and 19 %. The loss of solubility when a higher amount of fluorinated monomers was introduced prevented the synthesis of polymers with higher percentage of fluorinated units incorporation.

Analogous copolymers **16** were synthesized by the Stille polymerization of 1,2-bis(tributylstannyl)ethene **10** with variable ratios of the two aromatic monomers 1,4-diiodo-2,3,5,6-tetrafluorobenzene **9** and 1,4-diiodo-2,5-bis(octyloxy)benzene **17**, in the presence of Pd(0) catalyst and copper iodide (Scheme 8) [30]. When equimolar amounts of the two aromatic monomers were reacted, the percentage of tetrafluorophenylene units in the polymer was measured to be as high as 63 %, indicating a preferential incorporation of the fluorinated monomer, reasonably due to higher reactivity of the electron-poor aromatic bis-halide **9** compared to the alkoxy-substituted monomer **17**.

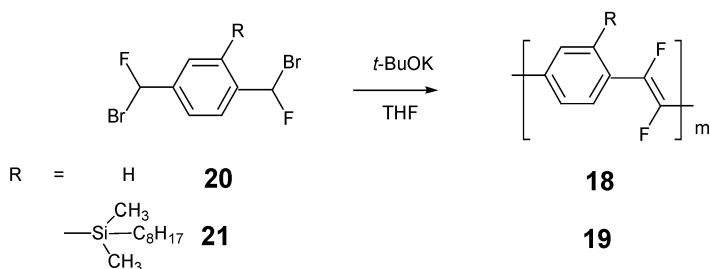


Scheme 8

The absorption spectrum of copolymer **16** measured on thin film showed two absorption bands with maxima at $\lambda_{\text{max}} = 440$ and 360 nm, which closely resemble the main absorption bands of thin films of the corresponding homopolymers (the parent alkoxy-substituted PPV $\lambda_{\text{max}} = 460$ nm, and the PTFPV **11** $\lambda_{\text{max}} = 350$ nm), thus evidencing the contribution of the two differently substituted PPV segments present in the copolymer. Thin film photoluminescence spectrum of **16** appears red-shifted also with respect to the parent alkoxy homopolymer, which suggests the presence of strong interchain interactions due to the coexistence of segments with complementary electronic effects. Photoelectrochemical investigation has also been carried out on copolymer **16**, demonstrating that the material can be electrochemically both *p*- and *n*-doped with different structures of positive and negative charge carriers [31].

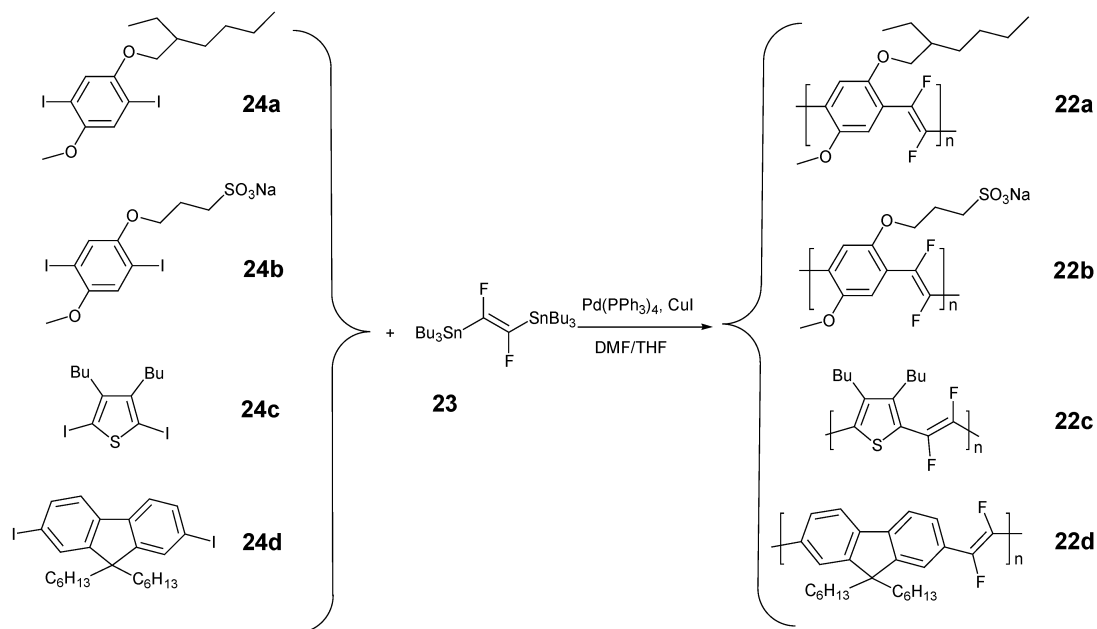
Third-order nonlinear optical properties were measured both in solution by the Z-scan technique [32] and in thin film by the third harmonic generation methodology [33]. A strong enhancement of the nonlinear $\chi(3)$ coefficient was detected in copolymer **16** in comparison with the parent homopolymers. This can be attributed to increased molecular polarizability caused by the simultaneous presence of aromatic rings bearing substituents with complementary electronic effects, which breaks the symmetry of charge distribution.

We have recently extended our investigation of the synthesis of fluorinated PPVs based on the Stille coupling to PAVs with fluorine atoms on the vinylene units. Introduction of fluorine atoms in the vinylene positions appears synthetically more demanding than the corresponding functionalization on the aromatic rings. Indeed, only two examples of PPV polymers with completely fluorinated vinylene units, **18** and **19**, had been reported before our work, which were synthesized by the Gilch precursor route from bis(bromofluorobenzyl) derivatives **20** and **21**, respectively (Scheme 9) [34].



Scheme 9

Our approach to PAVs with fluorinated double bonds **22a–d** (Scheme 10) consists of a Stille polymerization involving the reaction of (*E*)-(1,2-difluoro-1,2-ethenediyl) bis[tributylstannane] **23** [35] with various aromatic dihalides **24a–d** [36].



Scheme 10

Besides PPV polymers **22a,b**, bearing either apolar or polar charged side chains, also a poly(thienylenevinylene) **22c** and a poly(fluorenevinylene) **22d** fluorinated on double bonds were obtained.

Noticeably, the molecular weight of the polymers **22a–d** obtained using the fluorinated vinylene bis stannyl reagent **23** were considerably higher than those typically achieved in the corresponding reactions carried out with the nonfluorinated vinyl bis(stannane) **10**. However, the most significant consequence of the functionalization of double bond with fluorine atoms is represented by the strong hypsochromic shift of both the absorption and emission spectra in solution, which is also maintained in the solid state. In this respect, the comparison of emission spectra maxima of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV), one of the most widely used red–orange emitter of the PPV family (555 nm in solution, 562 nm in solid state), is particularly noteworthy, with the emission maxima of its fluorinated counterpart **22a** (466 nm in solution, 453 nm in the solid state). The latter represents the bluest solid-state emitting poly(*p*-phenylenevinylene) reported so far. Also, polymers **22b** and **22d** turned out to be blue-emitting polymers. In light of these data, the introduction of fluorine atoms on double bonds can be considered an effective structural modification toward strongly blue-shifted emission of PAVs both in solution and in the solid state, resulting in a new class of blue-emitting materials. On the basis of theoretical calculations and spectroscopic measurements, the observed blue-shift can be attributed to distortion of the conjugated backbone, which is induced by steric repulsion between the fluorine atoms on the vinylene units and the neighboring alkoxy substituents on the aromatic rings [37].

CONCLUSIONS

Our recent contribution in the development of synthetic methodologies for functionalized conjugated polymers, based on Pd-catalyzed coupling reactions of organometallic derivatives, has been briefly overviewed.

PAEs functionalized with D-glucose **1a–e** or L-phenylalanine **6** molecules as chiral substituents have been obtained by coupling of aromatic bis halides with bis(trimethylsilyl)ethynyl benzenes. In the case of the amino acid-substituted PPE **6**, the chirality of the biomolecules bounded as substituents has been demonstrated, to induce chiral supramolecular arrangement of the polymeric chains in the solid state, with interesting consequences on photoluminescence properties. Furthermore, both the glucose and the amino acid-substituted PPEs **1a** and **6**, respectively, have been used as active layers in quartz crystal microbalance gravimetric chiral sensors able to discriminate menthol enantiomers in the vapor phase.

PAVs functionalized with fluorine atoms either on the aromatic rings **11** and **13** or on the vinylene units **22a–d** have been synthesized by the Stille cross-coupling reaction between bis(stannyl)ethynyl derivatives and aromatic bishalides. This organometallic methodology appears advantageous, in many respects, in comparison with the soluble precursor routes used to yield similar polymers. Effects of substitution with fluorine atoms, such as improved electron transport properties and blue-shifted emission, have been detected in the PPVs fluorinated with different substitution patterns. PPV **22a** with fluorinated double bonds and alkoxy groups on the vinylene units represents the bluest-emitting PPV polymer reported so far.

The examples discussed highlight the key steps in the development of tailored organic semiconductors from molecular design and synthetic methodologies to solid-state properties in view of different target applications.

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