Fluorinated organic materials for electronic and optoelectronic applications: the role of the fluorine atom

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In this article we highlight, by means of selected examples drawn from work performed in our or other laboratories, the features of some classes of fluorinated conjugated materials and their use in electronic devices such as electroluminescent diodes or field effect transistors. A variety of fluorinated conjugated systems, either molecular or polymeric, such as poly(phenylenevinylene)s, poly(phenyleneethynylene)s, polythiophenes, polyphenylenes, are dealt with. Attention is also focused on a different class of electroluminescent compounds, represented by the cyclometalated iridium complexes with various forms (*mer* and *fac*). In particular, fluorine atoms lower both the HOMO and LUMO energy levels. Consequently, the electron injection is made easier, the materials display a greater resistance against the degradative oxidation processes and organic n-type or ambipolar semiconducting materials may result. Moreover, the C–H···F interactions play an important role in the solid state supramolecular organization, originating a typical π-stack arrangement which enhances the charge carrier mobility.

Introduction

Special interest attaches to several classes of fluorinated molecules such as pharmaceutical compounds[1] and functional materials[2] of importance in various applied fields.

The specific features of fluorinated compounds are related to the halogen atom properties such as the high electronegativity (in the Pauling scale EN = 4), responsible for the strong polarization of the carbon–fluorine bond and for the high bond energy (*ca.* 480 kJ mol^{-1}). Besides the great thermal and oxidative stability, which should lead to a higher life of the devices, fluorinated organic compounds have a series of interesting features which can be summarized as follows:[3]

(i) Enhanced hydrophobicity and lipophobicity in perfluorinated substances.

(ii) An inverted charge density distribution in fluorinated aromatic compounds, the ring being the centre of positive charge, with respect to the corresponding hydrocarbons. This is a result of the balance between the negative inductive effect and the positive mesomeric effect of the halogen atom.

(iii) F···H–C interactions, similar to a hydrogen bond, but with a much lower energy, are present in fluorinated organic compounds. Although there is not a precise understanding of these interactions, they may play an important role in the solid

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state organization of fluorine compounds bearing both C–F and C–H bonds or between perfluorinated and hydrocarbon compounds.

In the past two decades a broad variety of polyconjugated organic materials characterized by semiconducting properties has been developed[4] for applications in many electronic devices such as organic light-emitting diodes (OLEDs),[5] organic thin film transistors (OFETs),[6] photovoltaics,[7] and sensors.[8] Different material typologies including oligomers, polymers, molecular compounds and organometallic metal complexes have been prepared and each of them is appropriate for one or more particular devices according to its electronic and structural features (*e.g.* energy band gap or HOMO–LUMO energy levels, positive and negative charge carrier mobilities, crystallinity degree, thermal or oxidative stability). All these characteristics are affected by the nature of the substituents introduced on the conjugated system, and fluorine atoms may confer distinctive qualities, as reported above.

In particular, the introduction of electron-withdrawing substituents such as fluorine atoms is expected to lower both the LUMO and HOMO levels[9] in polyconjugated systems facilitating the electron injection. Therefore, fluorinated compounds may play a primary role as active materials in OLEDs and OFETs because they can behave as ambipolar or n-type semiconductors, contrary to the p-type nature of the corresponding non-fluorinated compounds. A relevant effect in conjugated systems bearing fluorine-substituted aromatic moieties is the π-stacked supramolecular organization in the solid state due to the strong interactions between the electron-poor fluorinated aromatic rings and the electron-rich non-fluorinated ones,[10] which may be present in the same[10b,d] or in a different molecule.[10a,e–i] These interactions are also operating in complex conjugated systems of oligothiophenes, oligoarylenes, and polynuclear aromatic compounds. The high ordered molecular stacks with an efficient overlap of π-orbitals may improve the charge transport ability for OFET applications.

In the following paragraphs the effects of the presence of fluorine atoms in some electroactive systems will be discussed. This paper cannot be considered an exhaustive review of the topic but just a presentation of selected examples, drawn from the work performed in our or others laboratories, highlighting the special features of the following classes of fluorinated materials:

1. Poly(phenylenevinylene)s (PPVs).
2. Poly(phenyleneethynylene)s (PPEs).
3. Polythiophenes.
4. Polyphenylenes.
5. Molecular materials.
6. Iridium organometallic complexes.

A choice has been made, considering only the examples in which the presence of fluorine atoms has an effective influence on the properties of the materials.

(1) Fluorinated PPVs

Poly(phenylenevinylene) and its derivatives have been the subject of much investigation, especially for their use as emissive layers in light-emitting diodes (LEDs). Two major issues are associated with this use of PPV polymers[5] and they can both be faced by the use of fluorine functionalization of the conjugated backbone. The first drawback is the poor stability of PPV polymers towards photo-oxidation of their double bonds, which reduces the devices' lifetime and, therefore, limits the possibility of a wide use in applications of commercial interest. The second problem is associated with a too high LUMO energy that makes PPV polymers poor electron-acceptors. As a consequence, the construction of efficient devices requires the use of low work function metals for electron injection, such as calcium, which is disadvantageous

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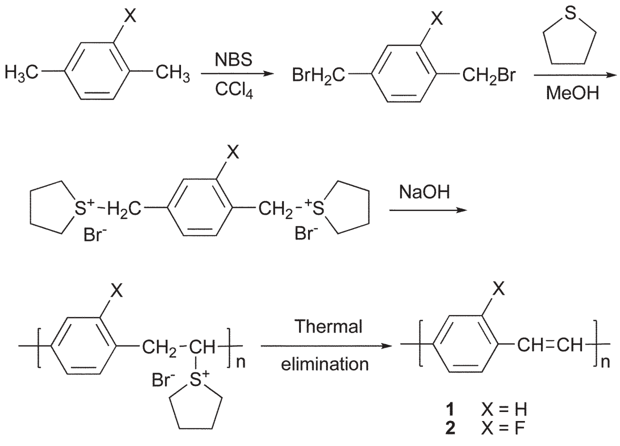
because of its high susceptibility to atmospheric degradation. The use of a more stable higher work function metal, such as aluminium, is desirable especially for commercial applications, but internal quantum efficiencies of PPV devices with indium tin oxide (ITO) hole-injecting and Al electron-injecting electrodes are no more than 0.01%. Calculations have shown that the introduction of an electron-withdrawing substituent onto either the aryl ring or the vinyl group of PPV would lower the HOMO and LUMO energy of the polymer, thus allowing the construction of more efficient devices with higher work function metals, such as aluminium. On these bases, the functionalization of vinylene units of PPVs with strong electron-withdrawing substituents, such as the cyano group, leads to efficiencies as high as 4% in bilayer devices with PPV as a hole-transporting layer and an aluminium electrode.

In consideration of the similarity between the electronegativity of fluorine atoms and cyano groups, it was expected that fluorine substitution could lower the LUMO and HOMO energy states, so that the electroluminescence (EL) efficiency would be enhanced. Lowered HOMO energies would also result in increased oxidation potential and enhanced stability against photo-oxidation. In addition, the electron-withdrawing property of the fluorine atom is expected to shift photoluminescence (PL) and EL spectra. All of these potentialities prompted investigations on the synthesis and properties of PPV polymers bearing different kinds of fluorine substitution and, interestingly, some fluorine-substituted PPVs were also reported to show contrasting effects in spectral shifts, depending upon the synthetic pathway adopted.

First Karasz and co-workers[11] and then Shim's group[12] described the synthesis of poly(2-fluoro-1,4-phenylenevinylene) *via* the soluble precursor route, originally reported by Wessling for the unsubstituted PPV (Scheme 1).[4]

Shim and co-workers[13] compared the yellow-emitting poly(2-fluoro-1,4-phenylenevinylene) **2** with poly(1,4-phenylenevinylene) **1**, also obtained through the water-soluble precursor method. Absorption spectra of **2** showed a very slight blue-shift with respect to unsubstituted PPV **1** (absorption maxima at 410 and 415 nm, respectively). The small blue-shift observed in the fluorinated polymer could be ascribed to the electron-withdrawing effect of the electronegative substituent. The bandgap energies of **1** and **2** were determined from the absorption band edges, resulting in very similar values (2.36 and 2.38 eV, respectively). Interestingly, the emission of **2** (560 nm, green-yellow colour) was red-shifted compared to that of **1** (540 nm), and the PL intensity of **2** was stronger than that of **1**. A similar behaviour was observed in the EL spectra. As a tentative explanation for the red-shift observed, the authors assumed that excitons generated in **2** may be trapped in shallow trap states associated with charge separation between the polymer backbone and the highly electronegative fluorine atoms and that this donor–acceptor pair recombination process exhibits a longer wavelength emission in **2**.



Scheme 1

The operating voltages of **1** and **2** in an ITO/polymer/Al OLED configuration were 6 and 10 V, respectively, which indicates that the band offset between **2** and the positive electrode (ITO) is higher than that of **1**. On the contrary, the relative EL quantum efficiency of **2** was 10 × higher than the corresponding value of **1**. This result may be due to the smaller band offset between the aluminium and the LUMO of **2** as compared with that in **1**, since the device quantum efficiency depends inversely on the energy barrier of the minor carrier (electrons in this case) injection.

In the light of these experimental results, the conclusion was reached that the electron-withdrawing fluorine atom in phenylene rings lowers the LUMO and HOMO states of **2**, without substantially changing the band gap values, thus facilitating electron injection from the Al electrode.

In another report, Lathi, Karasz and co-workers[14] described the photoluminescence and electroluminescence properties of the monofluoro-substituted polymer **2** (Fig. 1). Absorption maxima at 422 nm and emission maxima at 560 nm (identical to the values reported in the work of Shim and co-workers[13]) were recorded. The investigation was extended to the properties of 2,5-disubstituted PPV polymers, bearing two fluorine atoms per phenylene ring **3** or one fluorine atom and an alkoxy-substituent per phenylene ring **4**. These polymers were synthesized according to the same protocol used for the monofluoro-substituted PPV.

The electroluminescence of the polymers was studied both in a one-layer ITO/polymer/Ca and in a double-layer ITO/PPV/polymer/Ca OLED configuration using PPV as the hole-injection layer. The turn-on voltage of the single layer LED of the alkoxy-fluoro PPV **4** was just over 4 V, lower than the 6–7 V turn-on voltage measured in OLEDs fabricated using more electron-deficient monofluoro- and difluoro-substituted PPVs.

The difluoro-substituted PPV **3** has a UV-vis maximum very similar to that of the monofluoro-substituted polymer **2**, at 420 nm, but its PL and EL emission appeared considerably red-shifted with maxima at about 590 and 600 nm, respectively, yielding an overall reddish-orange emission colour. The

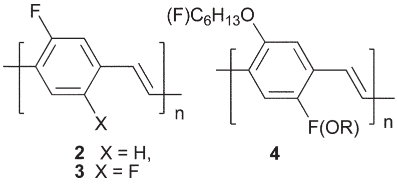


Fig. 1

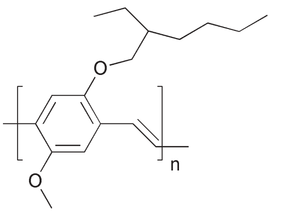


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Fig. 2

push–pull alkoxy-fluoro-substituted polymer **4** shows a UV-vis absorption maximum at about 450 nm and PL and EL emission considerably red-shifted at 630 and 610 nm, respectively, giving a red to reddish-orange colour. All the observed spectral shifts were attributed to electronic effects of the substituents.

The reddish electroluminescent polymer MEH-PPV[15] **5** (Fig. 2) has an emission at about 600 nm, very similar to that of difluoro PPV **3**. Actually, as a general rule, all the PPV derivatives with 2,5-disubstitution of mesomeric-donating, inductive-withdrawing substituents have a considerable red-shift relative to the PL and EL of the parent PPV in the solid state. Difluoro PPV **3** also has the longest wavelength luminescence of the series of PPVs substituted in the 2- and 5-positions with bromine, chlorine and fluorine atoms (Br 560 nm, Cl 580 nm, F 600 nm, respectively).[16]

The synthesis of a PPV with completely fluorinated aromatic units, namely poly(2,3,5,6-tetrafluorophenylenevinylene), has attracted considerable attention since the 1990s. Such a synthesis was unsuccessfully attempted *via* both water-soluble and organic solvent-soluble precursor routes by Brooke and Mawson in 1990.[17] In 1996, a report by Avny, Neumann and co-workers described the synthesis of a series of copolymers with phenylenevinylene (PPV) and tetrafluorophenylenevinylene (TFPV) units **6** (Fig. 3) *via* the Wessling route.[18]

A decrease in both conversion and yield of the final polymer was observed when the more fluorinated monomer was used, so that it was impossible to obtain the fluorinated homopolymer – a 60% tetrafluorophenylene was the maximum percentage of fluorinated units incorporated to afford the final polymer in reasonable yield. The UV-vis absorption spectra of the copolymers showed a strong blue-shift, up to 60 nm, with respect to PPV, as a function of fluorine content, which could be explained as a result of the inductive electron-withdrawing effect of fluorine atoms. On the other hand, the photoluminescence spectra of the copolymer appeared substantially unchanged in wavelength with respect to PPV, whereas a significant decrease of up to two orders of magnitude was observed in the photoluminescence intensity when comparing copolymers with 1–60% TFPV content. These effects were attributed to the very weak photoluminescence of the tetrafluorophenyl segments with respect to the phenyl counterparts which, therefore, dominate the emission spectra of the copolymers.

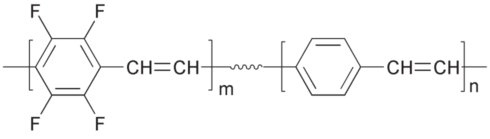

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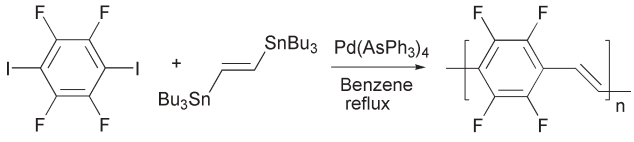
Fig. 3



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Scheme 2

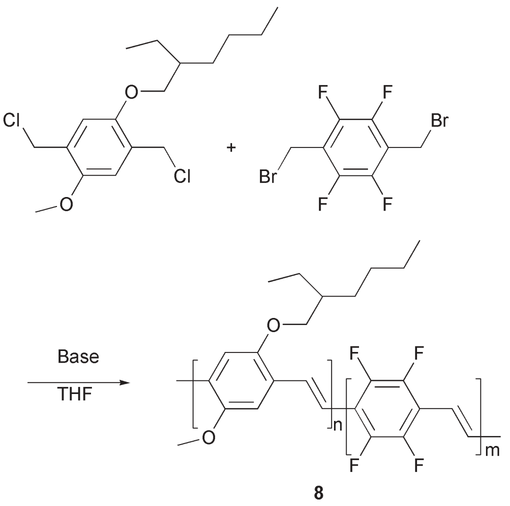
Electroluminescence of the copolymers with 10, 20 and 60% fluorinated monomer content was measured in the simple ITO/polymer/Al configuration. Dc voltages of up to 30 V did not yield any emission. Electroluminescence was therefore measured by applying an ac voltage (12 V rms at 600 Hz) and the spectra obtained under these conditions showed a slight blue-shift by increasing the fluorine content. According to the explanation reported, TFPV and PPV segments may have similar EL efficiencies, but the higher threshold function for TFPV makes these segments weak EL-emitting chromophores in the copolymer. Therefore, the net effect of increasing the TFPV content is a blue-shift of about 60 nm in the UV-vis absorption due to the electron-withdrawing effects of fluorine atoms, but of only 15 nm in the EL spectrum due to shortening of the PPV segments which dominate the EL emission.

However, the high threshold voltages, together with the weak luminescence, renders these devices of no practical utility.

In 2001 we published the first synthesis of the homopolymer[19] **7**, based on an organometallic approach involving the Stille cross-coupling reaction of 1,4-diiodotetrafluorobenzene with *trans*-1,2-bis(tributylstannyl)ethylene, under Pd(0) catalysis (Scheme 2).

The product, although insoluble in common organic solvents, was fully characterized by MALDI-TOF mass spectrometry. IR spectroscopy allowed the assignment of the *trans*-configuration to the vinylene units. Thin films of the polymer could be obtained by thermal evaporation under high vacuum, and absorption and emission spectra were recorded, showing emission in the green region of the spectrum. Single-layer electroluminescent devices, fabricated using **7** as the emitting layer, aluminium and ITO as cathode and anode, respectively, did not yield any emission even at high current density. This observation can be explained in terms of a high energy barrier for hole injection from the ITO anode, while a significantly lower energy barrier is expected for electron injection from the Al cathode into the conduction band of polymer **7**. In fact, the introduction of a hole-transporting TPD [*N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine] layer between the ITO anode and the polymer **7** resulted in a green-emitting device with a threshold voltage of 6.5 eV.

Few months later Gan *et al.*[20] reported the synthesis of **7** by a modified soluble precursor route, namely the bromine precursor route (BPR). However, the material obtained was not structurally ordered as **7** prepared *via* the organometallic approach, since both *cis* and *trans* double bonds were detected in the polymer, and trace amounts of unconverted precursor units were also revealed by elemental analysis. The latter



Scheme 3

structural feature may be responsible for the multi-peak characteristics observed in the PL spectrum (two broad peaks with maxima at around 465 and 500 nm and a shoulder at around 440 nm). The polymer obtained by BPR was used as the active layer in a simple ITO/polymer/Al configuration OLED which was driven with direct current and showed green emission with a turn-on voltage of about 4.2 V.

The functionalization of the PPV backbone with both electron-donor (alkoxy) and electron-acceptor (cyano) groups was demonstrated to be an effective strategy to improve the efficiency of light-emitting diodes made up with these polymers, because this functionalization modifies both the HOMO and LUMO levels in the right direction to balance charge injection from the electrodes.[21]

In 2000 Cacialli's group[22] reported the synthesis of random copolymers of fluorine- and alkoxy-substituted poly(*p*-phenylenevinylene) **8** by the Gilch-type polymerization of bis(halomethyl)phenylenes in THF (Scheme 3).

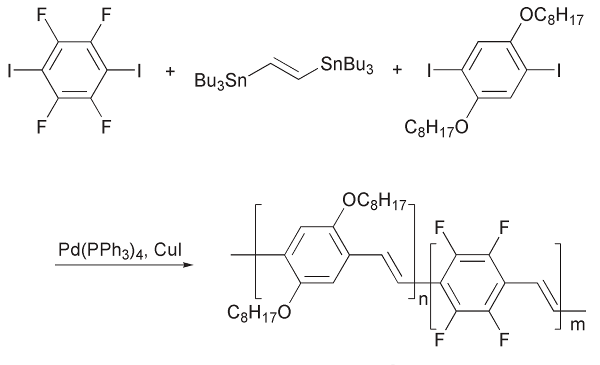
The fluorinated and the alkoxy-substituted units were used in different ratios, thus obtaining various copolymers incorporating fluorinated monomers in 7, 14 and 19% weight ratios. The synthesis of polymers with higher levels of fluorine incorporation was prevented by the loss of solubility observed as the fluorine monomer percentage was further increased in the polymerization process, leading to a completely insoluble material.

Electrochemical measurements showed an increase of the oxidation potential with fluorine content, as expected for the electron-withdrawing effect of fluorine on the conjugated π-electron system.

The absorption spectra of the resulting polymers were relatively independent of the fluorinated unit percentage (only a very small blue-shift was observed), which is quite surprising, considering that a more than 50 nm blue-shift of the absorption maximum was observed in going from 1 to 30% TFPV content in the copolymer **6**.[18] The discrepancy was attributed to a number of factors including an "electronic buffer" effect that could be due to the alkoxy chains, compensating or neutralizing the effect of the fluorine atoms. In fact, Lathi, Karasz and co-workers[14] demonstrated that the addition of an alkoxy chain onto the phenyl ring of **2** (Fig. 1) can effectively red-shift the spectrum.

The photoluminescence quantum efficiency appeared considerably reduced in comparison with that of MEH-PPV **5** obtained by the same methodology. It ranges from 4.2 to 6.7% in the copolymers **8** *vs.* 14% for MEH-PPV. OLED devices were fabricated in a two-layer configuration, with a PEDOT:PSS hole injection/transport film between ITO and the luminescent polymer. The electroluminescence efficiencies of the copolymers were about one order of magnitude lower with respect to MEH-PPV **5** using the same cathode metal (Ca), and they were found to decrease with increasing fluorinated unit percentage. Also reported was an increase of the devices' turn-on voltages with fluorine content. The electrical characteristics of LEDs with Al electrodes show that lower fractions of TFPV result in higher currents. Furthermore, current densities in MEH-PPV **5** are lower than in the fluorinated copolymers. Introduction of a hole-blocking layer between copolymers **8** and the Ca cathode resulted in lower currents and a 40% increase in device efficiency. It is interesting to note that PL and EL efficiencies do not correlate. Indeed, whereas the PL efficiencies of the copolymers are between one-half and one-third of that of MEH-PPV **5**, the maximum EL efficiencies are only between 14 and 6% of that of MEH-PPV **5**.

Soluble random copolymers of 2,3,5,6-tetrafluorophenylenevinylene and 2,5-dialkoxyphenylenevinylene **9**–**11** reaching percentages of tetrafluoro-substituted phenylene units higher than 60% were synthesized by the Stille cross-coupling reaction of 1,2-bis(tributylstannyl)ethylene and variable ratios of the two aromatic monomers 1,4-diiodo-2,3,5,6-tetrafluorobenzene and 1,4-diiodo-2,5-bis(octyloxy)benzene, using tetrakis-(triphenylphosphine)palladium(0) as the catalyst in the presence of copper iodide (Scheme 4). We attributed the solubility of copolymers with such a high percentage of fluorinated units, compared with the results concerning the work of Cacialli's group, to the considerably lower molecular weights of the polymers obtained with the strategy described in our work. Three different copolymers **9**, **10** and **11** were obtained by changing the feed ratio of the two aromatic monomers.[23] A detailed investigation was reported for the copolymer **10** obtained using an equimolar feed ratio of the



9	co[TFPV-DOPV]	Feed ratio 20:80
10	co[TFPV-DOPV]	Feed ratio 50:50
11	co[TFPV-DOPV]	Feed ratio 65:35

Scheme 4

two aromatic monomers.[24] A preferential incorporation of the tetrafluoro-substituted monomer (63 : 37 percent ratio of fluorinated aromatic monomer *vs.* the alkoxy-substituted counterparts) was estimated in the resulting product by ^{1}H NMR spectroscopy.

The absorption spectrum of copolymer **10** showed two resonances, at $\lambda = 440$ and 360 nm, close in energy to the main absorption bands of the corresponding homopolymers (DOPV $\lambda = 480$ nm, TFPV $\lambda = 347$ nm) suggesting the presence of the two differently-substituted chain segments randomly arranged in the structure of the copolymer. The slight shifts in energy observed for both the transitions can be ascribed to the interaction of adjacent segments with acceptor and donor substituents. The UV-vis absorption spectra of **9**, **10** and **11** show that the blue-shift of the main absorption band increases with the fluorinated unit percentage (480.3, 466.5, 445.0 nm), while the absorption due to the fluorinated segments increases in intensity.

Thin film photoluminescence spectrum of **10** was also compared with those of the two homopolymers. The red-shift observed for **10** with respect to the parent homopolymer suggests a much higher formation of interchain species in the copolymer, due to the coexistence of segments with complementary electronic effects, which should promote, in the solid state, strong interchain interactions.

Third-order non-linear optical properties (non-linear refractive index and two-photon absorption coefficients) of the push–pull substituted copolymers were measured at 1064 nm by the picosecond Z-scan technique in chloroform solution, to study their dependence on the copolymer composition. All the investigated substituted PPVs exhibit a small two-photon absorption coefficient, almost independent of the relative concentration of the two kinds of aromatic rings. On the other hand, the non-linear refractive index is negative and very sensitive to this ratio. A very large $n_2 = (-10 \pm 2) \times 10^{-12}$ cm^2 W^{-1} was measured for the copolymer obtained using an equimolar feed ratio of fluorine- and alkoxy-substituted aromatic monomers, which is one order of magnitude larger than the value measured in the corresponding homopolymer with only dialkoxy substitution. According to a tentative explanation, the simultaneous presence of fluorine- and alkoxy-substituted aromatic rings can lead to a large enhancement of $\chi(3)$ due to an increased molecular polarizability connected with symmetry breaking in the charge distribution.[25] Enhancement of third-order non-linear optical properties in copolymer **10**, due to the simultaneous presence of electron-withdrawing fluorine atoms and electron-donating alkoxy groups, with respect to the corresponding homopolymers TFPV and DOPV was observed also in thin film measurements of $\chi(3)$ coefficients by the third harmonic generation technique.[26]

Copolymer **10** was also subjected to a detailed electrochemical and photoelectrochemical investigation,[27] and the infrared active vibration (IRAV) band patterns for electrochemically p- and n-doped copolymers were found to be different, indicating the existence of different structures of positive and negative charge carriers during electrochemical doping. The photoinduced IRAV bands were found to be more similar to those obtained during electrochemical reduction (n-doping), in contrast with most of the other conjugated polymers, which show analogies with oxidation (p-doping) IRAV bands. This is the first example reported of a p- and n- dopable polymer with different IRAV patterns of charge carriers of both signs, and a similarity between n-doping and photodoping IRAV bands.

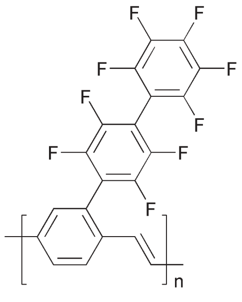


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Fig. 4

Not only fluorine atoms were tested as electron-withdrawing groups attached to PPV polymers, but also perfluorinated moieties. An example of this approach is given by the PPV **12** (Fig. 4) bearing perfluorinated biphenyl units as substituents on the aromatic rings.[28] The perfluorinated biphenyl unit was reported to be an efficient electron-capturing moiety, and it was used as a chromophore-blocking unit in a conjugated–non-conjugated multi-block copolymer.[29,30] Starting from this consideration, Shim and co-workers reported the synthesis of this material using the Wessling–Zimmermann approach, from a properly designed terphenyl building block.

The resulting conjugated polymer **12**, which showed an excellent thermal stability up to 400 °C in nitrogen atmosphere, presented absorption and emission maxima at 400 and 520 nm, respectively, corresponding to green light emission. Electroluminescence emission maxima, recorded both in the single-layer and in bilayer configurations, were about 520 nm, corresponding to a pure green light emission.

Polymer **12** also showed a higher turn-on electric field in comparison with the unsubstituted polymer, indicating that the band offset between **12** and a positive electrode (ITO) is larger than that of PPV. Therefore, the hole (major carrier) mobility should be restricted, resulting in balanced injection of holes and electrons. As a consequence, polymer **12** showed about 64 × enhanced EL efficiency compared with PPV, due to the electron transport ability of the electron-withdrawing perfluorinated biphenyl unit. Interestingly, the PPV/**12** double-layered device exhibited a much better EL efficiency and lower turn-on voltage than the PPFPV single-layered device (a 380-fold increase compared with PPV). These results are very consistent with the balanced injection of holes and electrons by the lower negative band offset of **12** as expected.

The trifluoromethyl group was also used as an electron-withdrawing group on the phenyl ring of two PPV polymers **13a**,**b** obtained *via* the bromine precursor route[31] (Fig. 5).

A slight blue-shift was observed for these polymers, in comparison with unsubstituted PPV obtained *via* the Wessling route. As expected, the blue-shift is higher in the case of the PPV without the alkoxy group. The double-layer OLED in the

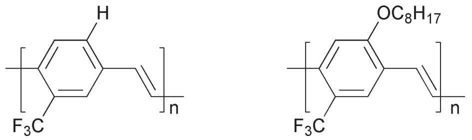

13a **13b**

Fig. 5

configuration ITO/PPV/**13b**/Al showed uniform emission with an EL internal quantum efficiency up to 0.01%, and no significant increase in the efficiency of the cells was observed by replacing Al with Ca, suggesting that the trifluoromethyl electron-withdrawing group is effective in improving electron injection. Poorer results were obtained in the case of the polymer **13a**, with a maximum efficiency of the order of 0.001%.

An important proof of the ability of perfluorinated side chains to enhance the photostability of the PPV polymers was offered by Kim and Swager, who reported the poly(phenylenevinylene) **14** with two trifluoromethyl moieties on the aromatic ring obtained by the BPR approach[32] (Fig. 6).

An alternating copolymer containing CF_3-PPV and MEH-PPV units **15** (Fig. 6) was also synthesized for comparison by Wittig condensation. The electron-withdrawing trifluoromethyl units contributed to a decrease in the rate of photobleaching in the copolymer, when compared to the MEH-PPV **5** homopolymer. In particular, the homopolymer **14** demonstrated a level of photostability unprecedented for a semiconductive conjugated organic polymer, which endows this material with the critical stability needed for optoelectronic devices and sensory applications.

Introduction of fluorine atoms on the vinylene units has also been reported as a possible strategy for increasing the electron affinity of PPV polymers, in order to reduce the energy barrier for electron injection. With this aim, poly(*p*-phenylenedifluorovinylene) **16** and poly(2-dimethyloctylsilyl-*p*-phenylenedifluorovinylene) **17** (Fig. 7), containing two fluorine atoms on each vinylene unit, were synthesized by Suh and co-workers.[33] The polymerization occurred *via* the Gilch protocol. The polymers were both soluble in various organic solvents and showed quite good thermal stability by thermogravimetric analysis.

Polymer **16** exhibits an absorption spectrum with a maximum peak at 390 nm, which is about 30 nm blue-shifted with respect to PPV, while the PL spectrum (λ_{max} 580 nm) is about 40 nm red-shifted in comparison with the value for PPV. On the other hand, the PL spectrum of **17** thin film exhibits a maximum at 495 nm, which is blue-shifted about 30 nm relative to that of **18**. The blue-shift in the spectroscopic features of **17** compared with those of **18** indicates the decrease of the effective conjugation length by the inclusion of the fluoro group at the vinyl position, possibly caused by the steric effect between the fluoro group and the bulky trialkylsilyl group.

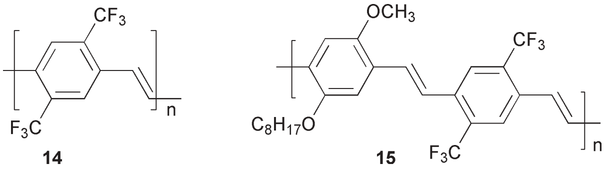

14 **15**

Fig. 6

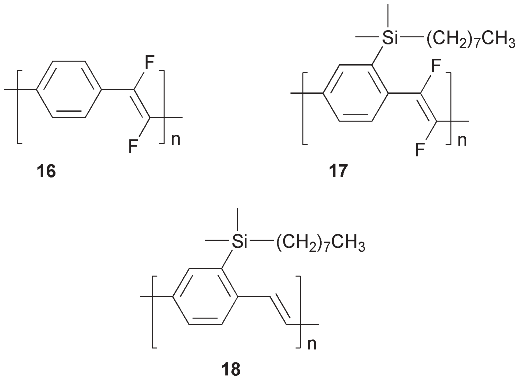

16 **17** **18**

Fig. 7

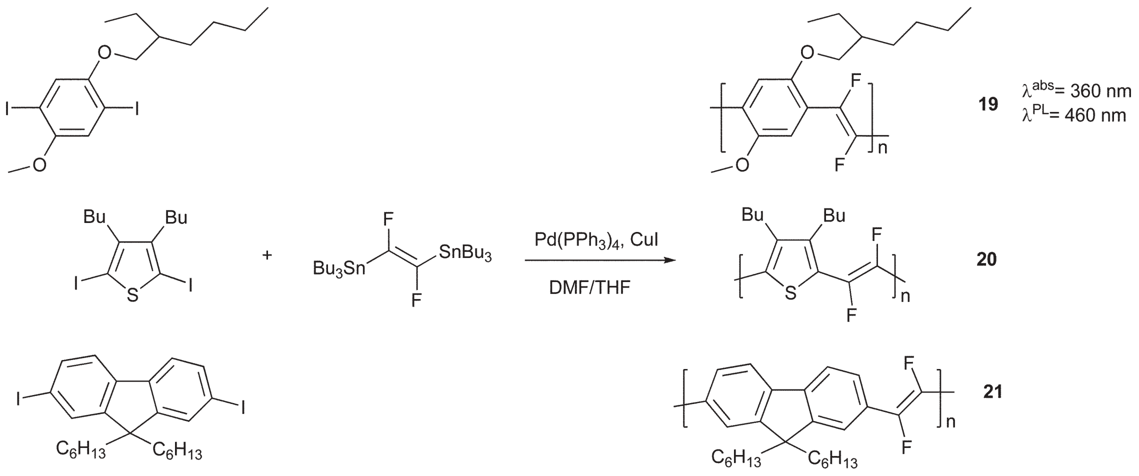
The band gap and the HOMO level for the two polymers, which were estimated from the absorption edges and from cyclic voltammetry, respectively, are 2.42 and 5.47 eV for **16**, and 2.7l and 5.51 eV for **17**. The HOMO and LUMO energy levels of **16** are lower than those of **17** (band gap 2.34 and HOMO level 5.04 eV), and this effect can be attributed to the introduction of the electron-withdrawing fluorine atoms on the vinylene units. The higher work function of the LUMO of **17**, compared with that of **18**, indicates that the electron injection process is easier in the former than in the latter compound.

Both the polymers synthesized were used as the electroluminescent (EL) materials in double-layer LEDs (ITO/PEDOT/polymer/Al). The EL spectra of **16** and **17** exhibit maximum peaks at 565 and 540 nm, which correspond to yellow and green light, respectively, with turn-on voltages of approximately 3–4 V. The efficiency of the LED made with **17** is about 7 × higher than that made with **18**, due to the higher work function of the LUMO of **17** than that of LUMO of **18**.

A general approach for the synthesis of soluble PPVs **19**–**21** with fluorinated vinylene units was recently developed in our laboratories, using the Stille cross-coupling reaction of (*E*)-1,2-difluoro-1,2-bis(tributylstannyl)ethene with various aromatic dihalides (Scheme 5).[34] Not only PPVs with fluorinated double bonds and alkoxy-substituted aromatic rings were obtained, but different poly(arylenevinylene)s such as thienylenedifluorovinylene **20** and fluorenedifluorovinylene **21**. In spite of the presence of electron-donating alkoxy groups on the phenyl rings of **19**, a strong blue-shift in both the absorption and luminescence spectra was observed, and our fluorinated version of the MEH-PPV **5** showed emission in the blue region of the visible spectrum. Further investigations on the physical properties of the fluorinated MEH-PPVs are still in progress.

(2) Fluorinated PPEs

Perfluorinated substituents on the poly(phenyleneethynylene) backbone were introduced in order to obtain PPE systems with high electron affinity. In particular, Swager's group proposed a modified version of the ultrasensitive sensory materials previously studied, based on pentiptycene-containing PPEs. These materials show fluorescence quenching as a response to



Scheme 5

vapours of electron-accepting analytes, such as 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT).[35] The detection mechanism exploited was the fluorescence quenching through non-bonding electrostatic associations between the electron-rich polymer and the electron-poor nitroaromatic quenchers. On this basis, the synthesis of electron-poor counterparts of the pentiptycene-substituted PPEs would result in materials sensitive to electron-rich aromatics, including compounds of biological importance, such as indoles and phenols. Therefore, PPEs **22** bearing [2.2.2] bicyclic ring systems incorporating electron-withdrawing perfluoroalkyl groups either on the pentiptycene moiety or directly on the aromatic rings of PPE systems were obtained[36] (Fig. 8).

The perfluoroalkyl substitution in the PPE system containing the pentiptycene moiety determines increased ionization potentials up to 0.50 eV, which can be tuned with the different substitution patterns. In agreement with the increased ionization potential, the materials show very good photostability. Sensing of electron-donating analytes by high ionization potential polymers was demonstrated by fluorescence quenching studies. Furthermore, tuning of ionization potentials by structural modifications could be used to impart dramatic selectivity changes in sensory responses.

In the framework of an investigation on the synthesis of poly(aryleneethynylene)s functionalized with glucose molecules, the copolymer **23**, bearing a regular alternation of phenylene units substituted with peracetylated glucose molecules and tetrafluorophenylene units, was synthesized by our research group, *via* a modified Cassar–Heck–Sonogashira coupling of glucose functionalized bis[(trimethylsilyl)-ethynyl] benzene with aromatic dihalides (Scheme 6).

The modified protocol, based on the use of silylated intermediates, was developed to reduce the homocoupling reactions typical of the cross-coupling process of ethynyl derivatives with aromatic dihalides.[37]

(3) Fluorinated oligo- and poly-thiophenes

Oligo- and poly-thiophenes, bearing either fluorine atoms directly bound to the polyheterocyclic system or perfluoroalkyl and semifluoroalkyl chains as substituents were reported. Self-assembling polythiophenes were obtained introducing semifluoroalkyl chains as substituents. Molecules consisting of both hydrocarbon and fluorocarbon segments of six or more carbon atoms [*i.e.* $H(CH_2)_m(CF_2)_nF$, where $m,n > 6$] form assemblies such as lyotropic mesophases and smectic-like structures, due to microsegregation arising from the

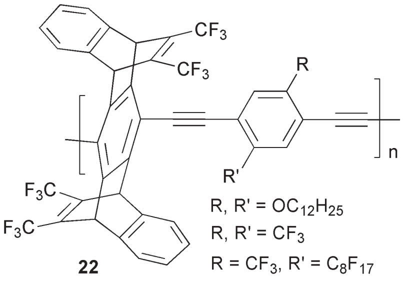
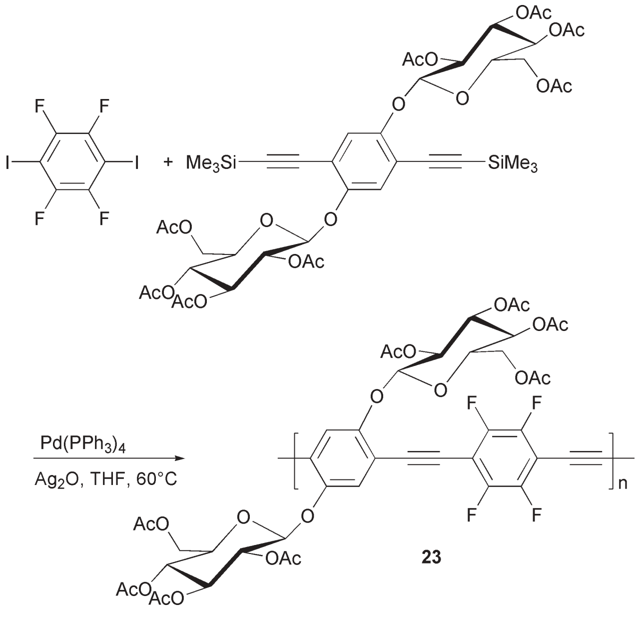
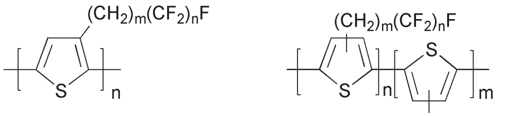


Fig. 8



Scheme 6



24 **25**

Fig. 9

immiscibility of fluorocarbons and hydrocarbons. Non-regioregular polythiophenes with a statistical head-to-head arrangement of semifluoroalkyl chains[38] **24** (Fig. 9) or random copolymers with alkyl and semifluoroalkyl chains **25** were obtained by oxidative coupling of the corresponding thiophenes substituted with alkyl or semifluoroalkyl chains.

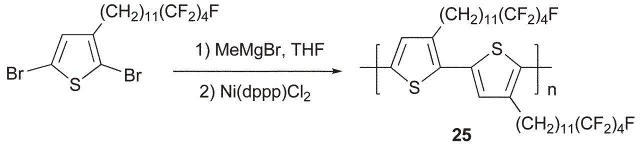
In this case, although the lack of regioregularity prevents an extended coplanarity of the thiophene backbone, the UV-vis spectra of polymers with a longer fluoroalkyl chain showed a more conjugated conformation in the solid state.

The amphiphilic nature of the semifluorinated chains was also evidenced by the formation of stable Langmuir–Blodgett monolayer films on silanized glass using the polyfluoroalkylthiophene **24** ($m = 3$, $n = 6$), obtained by chemical oxidation of the corresponding thiophene monomer. In this case the relatively high regioregularity of the polymeric chain (70% of head-to-tail linkages, calculated from ^{1}H NMR spectra) may facilitate a planar arrangement of the thiophene units in the monolayer, whereas the high hydrophobicity and rigidity of the $-CF_2-$ groups compared to $-CH_2-$ groups lead to a packing of the side chains oriented perpendicularly to the water surface. The Langmuir–Blodgett films showed a thermochromic behaviour with a shift to lower wavelength of the absorption band by increasing the temperature, as a consequence of conformational transitions which reduce the coplanarity of the conjugated chain.[39]

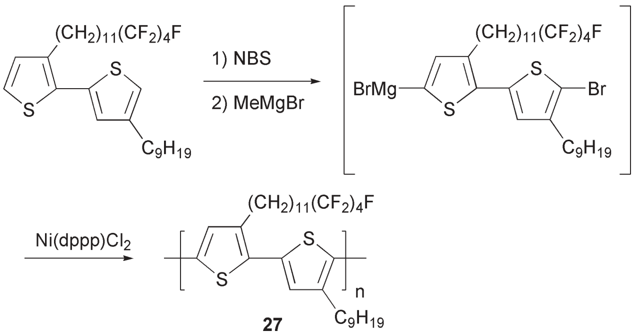
The oxidative methodology for the synthesis of polythiophenes affords polymeric materials with generally low regioregularity. On the other hand, the unique properties of hydrophobicity, rigidity and ability to induce aggregation of the fluoroalkylchains are expected to be maximized in high regioregular polythiophene fluoroalkyl derivatives.

Semifluoroalkyl-substituted polythiophene **25** was obtained with a head-to-tail linkage percentage higher than 95% (determined by ^{1}H NMR) by regioselective metallation of dibromothiophene derivatives by means of methylmagnesium bromide, followed by nickel-catalyzed cross-coupling of the resulting 2-bromo-5-bromomagnesium derivative (Scheme 7).

As expected, X-ray diffraction of thin films obtained by solvent casting of these materials revealed a great ordered structure: the thiophene rings are disposed in *anti* conformation with extended side chains in a lamellar phase. Moreover, owing to the presence of the mesogenic fluoralkyl chains, a liquid crystalline phase is evidenced by a thermochromic behaviour above 100 °C, with a shift of the absorption maximum to a shorter wavelength. This can be ascribed to a conformational change with a reduced coplanarity of the thiophene rings.[40]



Scheme 7

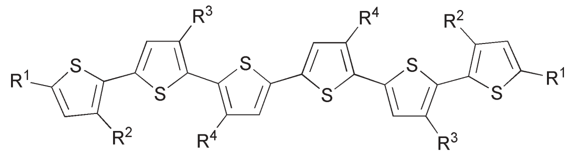


Scheme 8

The regioregular polythiophene copolymer **27** (Scheme 8) bearing alternating alkyl and fluoroalkyl side chains was also obtained starting from dibromobithiophene derivatives. Also in this case, a halogen–metal exchange occurred regioselectively on the bromine atom of the fluoroalkyl-substituted thiophene ring and the nickel-catalyzed polymerisation occurred with 90–94% of head-to-tail linkages.[41]

The X-ray diffraction pattern of a thin film of **27** cast from chloroform solution is quite different from that of the homopolymer **25** discussed above. In this case a highly ordered bilayer lamellar structure was observed in which the hydrocarbon side chains are packed together and are segregated from the semifluoroalkyl chains, which in turn are packed separately. These highly ordered and oriented structures may find potential applications in polarized electroluminescent devices or in field effect transistor (FET) fabrication.

In particular, FETs based on organic semiconductors may find niche applications in low-performance memory elements, sensors, pixel drive and switching elements in organic light-emitting diode displays. To achieve acceptable performances, organic semiconductors must satisfy stringent criteria related to the HOMO/LUMO energies for an easy charge injection, efficient charge migration, that is positively influenced by high purity of the material, preferential orientation of the long axis of the molecules perpendicular to the FET substrate, and single-crystal morphology of the material. In general, the properties of defined oligomers or molecular materials are more adherent to the above requirements, and oligothiophenes (*n*Ts) with a defined number of heterocyclic rings ($n = 4$–6) are among the most suitable materials for this application, due also to the high charge carrier mobility ($\mu = 4 \times 10^{-2}$ cm^2 V^{-1} s^{-1}). However, *n*Ts are mainly p-type semiconductors and, therefore, only positive charge carriers (holes) can be transported. The availability of n-type organic semiconductors would enable new applications such as bipolar transistors and p–n diodes besides a better understanding of the charge transport mechanism. Marks and co-workers have prepared a series of oligothiophenes (from 2T to 6T) bearing fluoroalkyl chains at the α,ω-positions **28**, at the β,β′-positions **30**, and in positions progressively displaced from the ends of

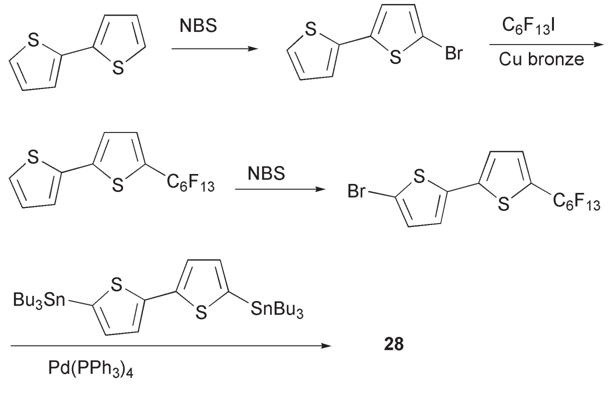


28 $R^1 = C_6F_{13}$; $R^2 = R^3 = R^4 = H$
29 $R^1 = C_6H_{13}$; $R^2 = R^3 = R^4 = H$
30 $R^1 = H$; $R^2 = C_6F_{13}$; $R^3 = R^4 = H$
31 $R^1 = H$; $R^2 = C_6H_{13}$; $R^3 = R^4 = H$
32 $R^1 = H$; $R^2 = H$; $R^3 = C_6F_{13}$; $R^4 = H$
33 $R^1 = H$; $R^2 = H$; $R^3 = H$; $R^4 = C_6F_{13}$
34 $R^1 = CH_2C_6F_{13}$; $R^2 = R^3 = R^4 = H$

Fig. 10

the conjugated core **32** and **33**, together with the corresponding oligomers with the simple alkyl chains **29** and **31** (Fig. 10).[42] The strategy adopted for the synthesis of these oligomers are the copper-promoted coupling of suitable bromo-oligothiophenes with perfluoroalkyl iodides, whereas the extension of the thiophene core is accomplished *via* palladium-catalyzed coupling of bromothiophene derivatives with stannyl or Grignard thienyl reagents, as reported in the Scheme 9 for the synthesis of **28**.

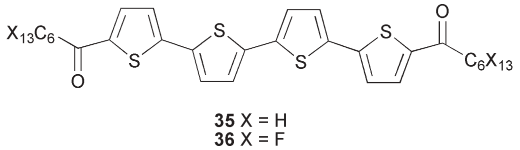
The fluoroalkyl oligothiophenes behave as n-type semiconductors whereas the alkyl-substituted oligothiophenes have a p-type character as the unsubstituted *n*Ts. FETs were assembled with thin films of both types of oligomers and charge carrier mobilities in the range 10^{-5} to 10^{-3} $cm^2\ V^{-1}\ s^{-1}$ were determined in the case of fluoroalkyl oligomers. However, film preparation modalities are of the utmost importance: the volatility of these materials allows the deposition of thin films by evaporation in high vacuum on a Si/SiO_2 substrate maintained at a constant temperature. Film growth at 25 °C indeed shows poor performance, whereas higher values of mobilities can be achieved by annealing to 60–80 °C or by direct deposition at these temperatures. On the other hand, the temperature deposition of films obtained from alkyl oligomers has a minimal influence on the charge carrier mobilities. XRD studies pointed out that, in the case of fluoroalkyl oligothiophenes, a crystallinity degree of films comparable with those of their alkyl counterparts can be obtained only by high-temperature growth or annealing. Moreover, as revealed by SEM analysis of these films, the grain dimension and interconnection increase dramatically with the growth temperature. The different behaviour of the fluoroalkyl oligomers in thin film formation can be in part caused by the high interconversion energy barrier between oligothiophene rotamers (in the case of the oligomer **30** about 12 kcal mol^{-1} larger than in the alkyl counterpart **31**), indicating that relatively stiff fluorocarbon chains have a stereoelectronic hindrance to planarization of the polyheterocyclic core at low temperature. The planarization is an important prerequisite, responsible for both high charge carrier mobility and for strong π–π interactions between the aromatic cores. The α,ω-substituted polythiophene **28** exhibits higher n-type values of μ with respect to the β,β′-regioisomer **29** and this feature can also be explained considering a decreased core conjugation due to a larger inter-ring torsion in this oligomer family. This hypothesis is supported by the very poor FET performance of films obtained from isomers with the fluoroalkyl chains in the middle thiophene rings **30** and **31**, which give rise to largely amorphous solid state structure. The n-type behaviour of the fluoroalkyl oligothiophenes with respect to the p-type character of the corresponding alkyl oligomers was ascribed to the electron-withdrawing capacities of the fluorocarbon substituents. Energy levels of the HOMO and LUMO orbitals in fluorinated and alkyl oligomers, evaluated from optical and electrochemical data, are located below and above those of the unsubstituted *n*Ts, respectively, and the lowering of the LUMO level appears to be an important feature for enhancing the electron-carrying ability of the fluoroalkyl oligothiophene. Electron- and hole-injection rates (R^{e^-} and R^{h^+}, respectively) were calculated taking the semifluoroalkyl oligothiophene **34** as a reference. This oligomer gives vacuum-deposited films with similar morphology to those of the fluoroalkyl ones but, being FET-inactive, is neither an n-type nor p-type charge carrier. The results of these calculations suggest that the charge carrier sign is dominated by the carrier injection characteristics rather than by the bulk transport properties, and high rates of electron injection were drawn for the fluoroalkyl-oligothiophenes. Therefore, the materials described show good performance in FET devices, which, however, must work only under high vacuum conditions. Recently, some structural changes have been introduced in order to improve the stability of the material and to fabricate OFETs working also in air.[43]



Scheme 9

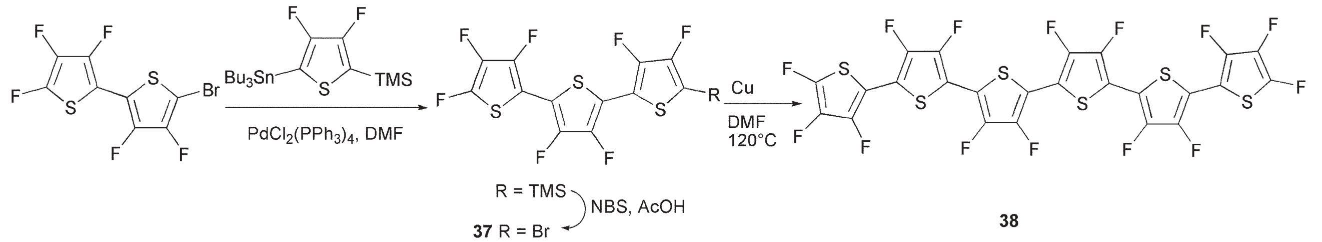
A carbonyl-functionalized quaterthiophene with perfluoroalkyl chains **36** (Fig. 11) and its alkyl counterpart **35** were prepared adapting the synthetic pathway previously described for the analogous perfluoroalkyl or alkyl derivatives.

The fluoro oligomer **36** has a n-type semiconducting character with very high values of electron mobilities in FETs working *in vacuo* and between 5 and 10× lower magnitudes in devices operating in air. Moreover, the hydrocarbon derivative **35** behaves as an ambipolar type semiconductor and exhibits



35 X = H
36 X = F

Fig. 11



Scheme 10

high values of electron mobility together with relatively large hole mobility. This oligomer is the first organic semiconductor with unoptimized μ_e/μ_h values as high as 0.1/0.01 $cm^2\ V^{-1}\ s^{-1}$.

Attempts to invert the p-type semiconducting oligothiophenes in good electron carriers were also made by introducing fluorine atoms directly onto the heterocyclic rings (Scheme 10).

The polyetherocyclic core was built up by Stille cross-coupling reaction to obtain the bromoperfluoroterthiophene **37** whose Ullmann coupling, using copper bronze, afforded the final product **38**.[44] A single crystal of the oligomer could be grown and the crystalline structure of the material was determined by X-ray analysis. The structure of the oligomer **38** is highly planar with all-*trans* conformation of the thiophene rings. The oligomer molecules adopt a π-stack structure with face-to-face molecules, which is expected to generate a high electron mobility along the π–π stacking direction. However, the HOMO–LUMO energy gap, as derived from absorption spectra and electrochemical measurements, is larger than that of the corresponding non-fluorinated oligomer and the LUMO level is at a higher value than expected through the presence of the fluorine atoms.[45] Other shorter oligothiophenes (Fig. 12) were synthesized following the same synthetic strategy.

Electrochemical and UV-vis-NIR data, coupled with theoretical calculations, show that also in this case the HOMO–LUMO gap energy values are slighty larger than the corresponding values of the unsubstituted oligothiophenes, and the introduction of fluorine atoms lowers the LUMO energy level; but this remains, however, still too high for the applicability of these materials in actual devices.[46]

The heavy influence of the solid state aggregation on the sign of the charge carriers and on their field-effect mobilities was highlighted in the perfluoroarene-thiophene oligomers **39**–**41** (Fig. 13), in which the perfluorophenyl rings are systematically displaced from the periphery of the conjugated system to the central positions of the oligomer core.[47] These materials were synthesized by Stille cross-coupling of the suitable thienylstannyl derivatives.

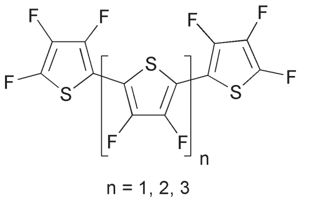


Fig. 12

The thiophene-fluoroarene small torsional angles in oligomers **39** and **40** (17.6 and 7.9° respectively) allow a nearly planar conformation of the thiophene-arene core. Molecular organizations of the oligomers **39** and **40** in the solid state are very similar to that of the perfluorohexathiophene with a π–π overlapped structure. This stacking is favoured by the interchain interaction of the fluorinated electron-deficient rings with the electron-rich thiophene rings. In oligomer **41** the large torsional angle (53.9°) between the adjacent fluoroarene rings prevents the planarization of the polyaromatic core and this does not allow a packing with an efficient π–π overlapping. In FET devices operating in moderate vacuum, the oligomer **39** is an n-type semiconductor. On the contrary, oligomers **40** and **41** are p-type semiconductors. Moreover, oligomers **39** and **40** show very high field-effect charge mobilities (0.08–0.01 $cm^2\ V^{-1}\ s^{-1}$), whereas oligomer **41** exhibits a much lower value ($4 \times 10^{-5}\ cm^2\ V^{-1}\ s^{-1}$). The different behaviour of **39** and **40** with respect to **41** may be explained by high planarization of the polyaromatic core in the solid state and a π-stacking which facilitates the intermolecular transport of the negative charge carrier. Another important factor may be the localization of charge in polaronic structures and the maximum charge separation would result in charge localization on the end rings,

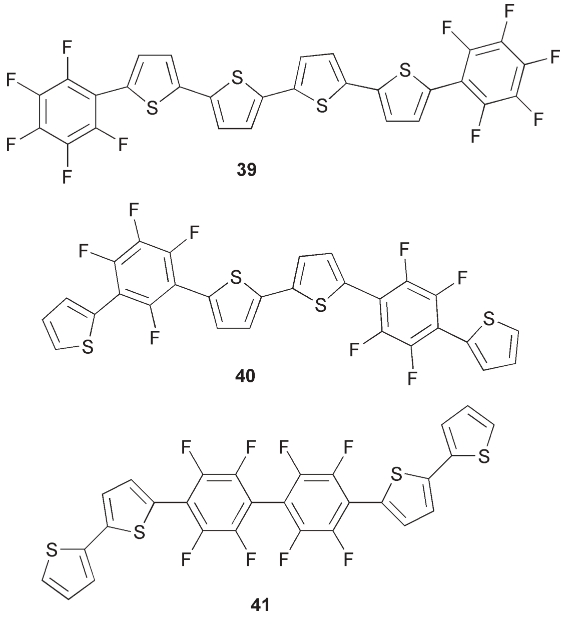
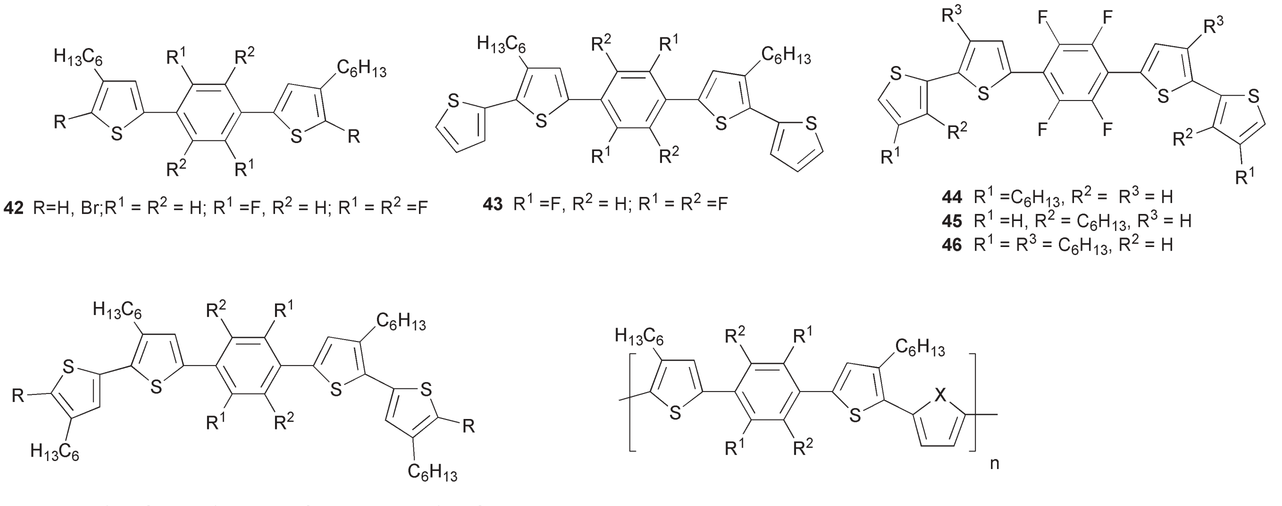


Fig. 13



42 R=H, Br;$R^1 = R^2 = H$; $R^1 = F$, $R^2 = H$; $R^1 = R^2 = F$

43 $R^1 = F$, $R^2 = H$; $R^1 = R^2 = F$

44 $R^1 = C_6H_{13}$, $R^2 = R^3 = H$
45 $R^1 = H$, $R^2 = C_6H_{13}$, $R^3 = H$
46 $R^1 = R^3 = C_6H_{13}$, $R^2 = H$

47 $R = R^1 = R^2 = H$; $R^1 = F$, $R = R^2 = H$; R = Br, $R^1 = R^2 = F$

48 $R^1 = R^2 = H$; $R^1 = F$, $R^2 = H$; $R^1 = R^2 = F$
X = S, Se

Fig. 14

fluoroarene ring for oligomer **39**, that should preferentially accommodate a negative charge, and thiophene ring for oligomer **40** that should have the opposite behaviour. The interactions of these factors may rationalize the electronic characteristics of these oligomers.

Several families of oligomers having one benzene nucleus in the central position of the polyaromatic system were prepared. In these compounds the benzene rings show an increasing number of fluorine atoms (up to four) (Fig. 14).[48]

Moreover, alkyl chains were introduced on the thiophene rings in order to improve the solubility. The synthesis was mainly based upon the Stille cross-coupling reaction.

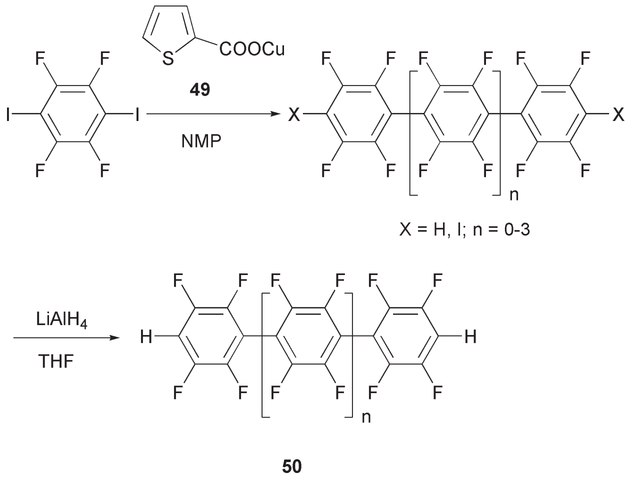
The comparison of the single-crystal or powder X-ray diffraction studies shows the presence of strong intramolecular H···F and S···F interactions that induce planarization of the polyaromatic core. This effect is very marked in the tetrafluorophenyl oligomer of each family, much reduced in the difluoro counterparts or absent in the unsubstituted compounds. The presence of alkyl chains in the tetrafluoro derivatives does not appear to twist significantly the coplanarity of the conjugated system. Computational studies pointed out that the fluorine atoms pull electron density out of the central ring, creating regions of positive and negative potential associated with the phenyl rings and thiophene rings, respectively. This electronic distribution facilitates the self-assembly of oligomers in a slip-stack arrangement with the phenyl ring of one chain facing two thiophene rings of two other chains, in order to optimize the interaction of the positive and negative regions. An out-of-plane extension of the alkyl chains encourages interplane interdigitisation and stabilizes the crystal phase. Moreover, the presence of fluorine on the central phenyl ring produces a strong stabilization of the HOMO level, confirmed by cyclic voltammetry measurements, which should make these systems less susceptible to oxidative degradation.

Oligomers **42** (R = Br) were polymerised by coupling with 1,4-bis(tributylstannyl)thiophene or 1,4-bis(tributylstannyl)selenophene.

The self-assembling ability operating in the parent oligomers is expected to be active also in the polymers **48**, giving structures with good charge carrier mobilities. Indeed, these materials were tested in FETs with thin films obtained by spin coating. All of these polymers are p-type semiconductors, in agreement with the results previously discussed for the arylene-thienylene oligomers with the fluorinated aryl ring in the middle of the structure. The charge carrier mobilities are in the range 2.6×10^{-4} to 1.3×10^{-5} cm^2 V^{-1} s^{-1} and in some case the annealing of the film duplicates the mobility, probably because annealing increases the structural order of the polymers at the interface with the dielectric layer, depending on the glass transition temperatures and viscosity. Very low mobilities were measured for polymers bearing non-fluorinated to partially fluorinated aryl rings (10^{-7}–10^{-6} cm^2 V^{-1} s^{-1}). The highest values of mobility were found for selenophene-containing polymers, and this may be due to the increase in intermolecular interactions between the polymer chains derived from the presence of the larger and more polarizable selenium atom. The materials reported in this work represent the efforts in transferring the self-assembling ability typical of oligomeric compounds to the polymeric ones, in order to obtain semiconducting organic materials for FET fabrication with good charge mobilities, good solubility and, hence, easy processability. Another relevant class of fluorine-substituted oligothiophene compounds is represented by photochromic 1,2-dithienylethene derivatives, decribed in a recent review.[49]

(4) Fluorinated oligo- and poly-phenylenes

Polyphenylenes (PPPs) and oligophenylenes are rigid rod-like molecules with p-type semiconducting properties. The relatively large band gap energy (about 3.0 eV) makes these materials blue-emitting electroluminescent candidates for OLED application. The unsubstituted PPP is almost insoluble in common organic solvents and, therefore, thin films were obtained from soluble unconjugated precursors which were



50

Scheme 11

successively converted into the conjugated materials. The introduction of alkyl or alkoxy chains on the polyaromatic structure increases markedly the solubility, but also increases the twist angle between the aromatic rings. Consequently, the conjugation length is reduced. Recently, oligomers with a defined length of the conjugation system have been proposed as an alternative to polydisperse materials owing to the possibility of obtaining thin films by evaporation under high vacuum.

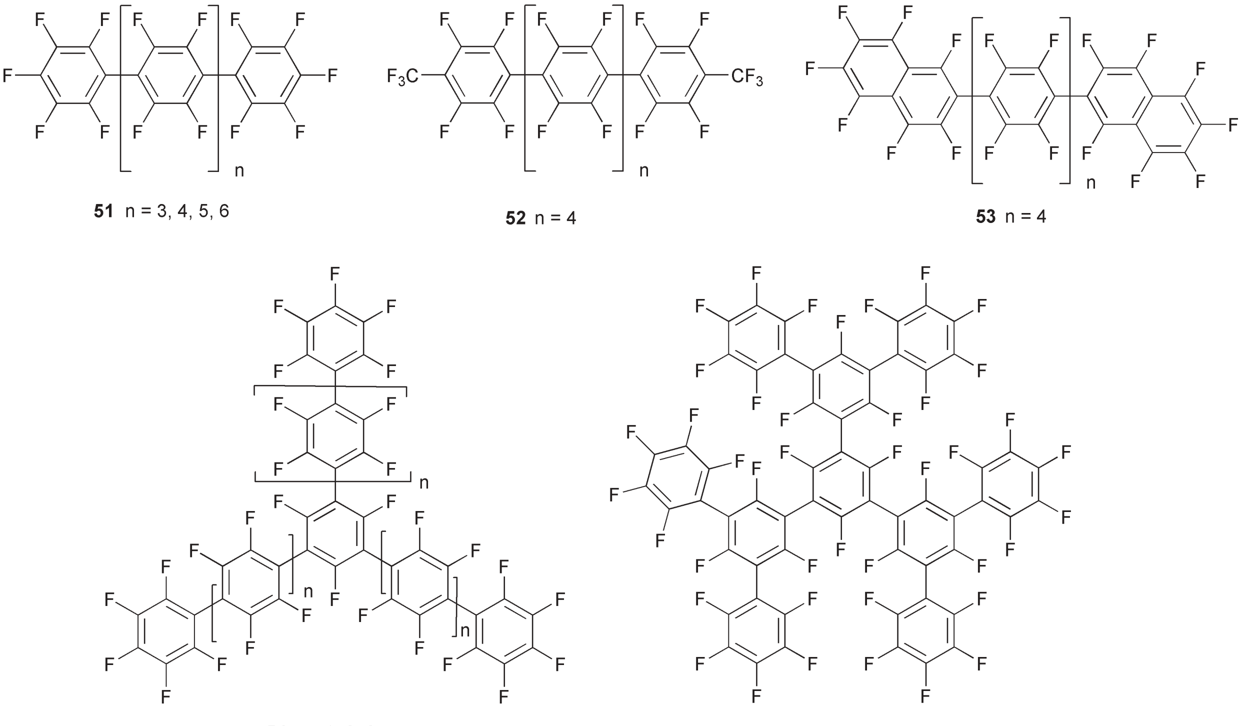
A simple procedure leading to fluorinated PPP oligomers is based upon the homocoupling reaction of 1,4-diiodo-2,3,5,6-tetrafluorobenzene (Scheme 11).[50] A complex mixture of oligomers containing up to five aromatic rings was obtained. A quantitative dehalogenation reaction with lithium aluminium hydride in THF led to the four-fluorinated PPP with hydrogen atoms as terminal groups **50**, which could be separated by flash chromatography.

The air-stable copper(I) thiophene carboxylate **49** was the specific promoter of this homocoupling reaction in *N*-methylpyrrolidinone as the solvent. Other copper(I) salts were ineffective.

More recently, perfluorinated oligophenylenes with linear,[51] dendrimeric,[52] or Y-branched[53] structure (Fig. 15) were prepared by simple coupling of fluoroarylcopper derivatives with fluorobromoarenes. A series of bromination and coupling steps performed sequentially allowed the build-up of oligomer structures.

These materials are interesting mainly in the field of electroluminescent devices. Their low-lying LUMO and HOMO levels facilitate the electron injection and, at same time, they may act as hole-blocking materials. Moreover, they are characterized by a relatively low sublimation temperature, which allows the preparation of thin films by thermal evaporation, and by high thermal and chemical stability due to the replacement of C–H bonds with stronger C–F bonds.

The main application of these materials is as electron-injecting, hole-blocking layers in OLEDs. The organic materials used in the OLED fabrication are mainly p-type semiconductors and transport holes more efficiently than electrons. Therefore the recombination of charges takes place near the cathode, resulting in quenching of the excitons produced. To overcome this drawback, a layer of these oligomers is interposed between the cathode and the emitting material in order to facilitate the electron injection and to relegate holes in the emitting layer. Materials used in the fabrication of OLEDs should be substantially amorphous in



51 n = 3, 4, 5, 6

52 n = 4

53 n = 4

54 n =1, 2, 3

55

Fig. 15

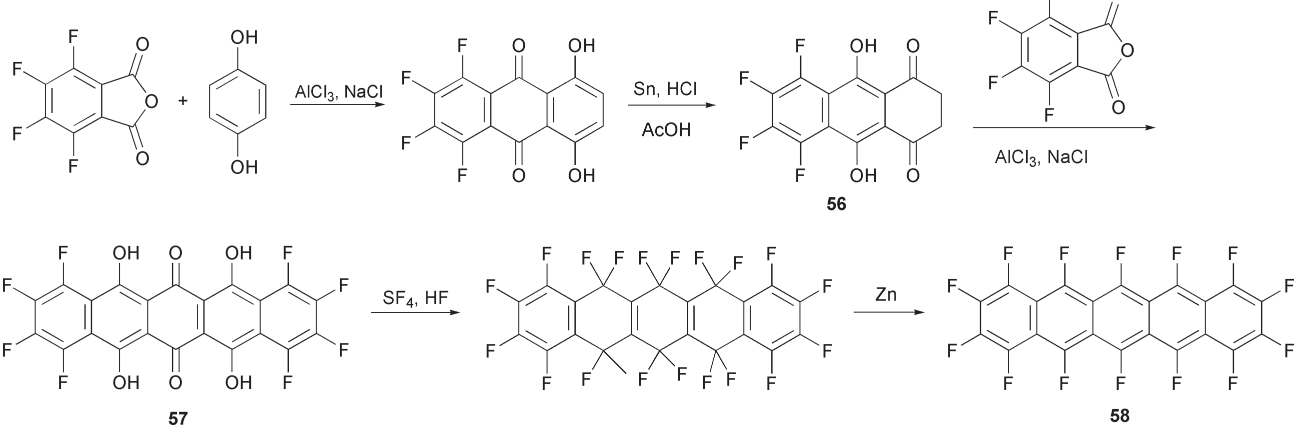
the solid state to optimize the performances of the devices. Dendrimer **55** and linear oligomers **51**, **52**, and **53** are insoluble in common organic solvents, and their solid state is highly crystalline as indicated by the sharp melting transitions without glass transition detected by differential scanning calorimetry (DSC). On the contrary the Y-branched oligomers **54** are stable amorphous solids, soluble in THF and $CHCl_3$, with relatively high glass transition temperatures (135–176 °C) and no melting transitions. The electron mobilities for Y-branched oligomers, determined by the time-of-flight technique are in the range 8.8×10^{-5} to 2.3×10^{-4} $cm^2 V^{-1} s^{-1}$ and are relatively high for amorphous n-type semiconductors. The hole-blocking ability was valued in OLEDs made with Alq_3 as the electroluminescent material, measuring the luminance–voltage characteristics in devices with and without a hole-blocking layer made with these oligomers. The best results were obtained with the Y-branched and linear oligomers with luminances in the range 4300–19 900 cd m^{-2} at relatively low voltages (10–20 V).

(5) Fluorinated molecular materials

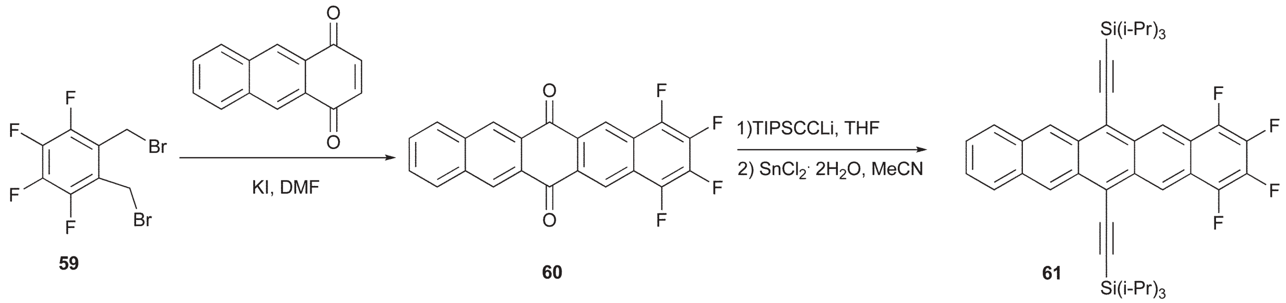
Polynuclear aromatic compounds such as anthracenes, pentacenes and perylenes were used as semiconducting materials mainly in FETs owing to their relatively high charge carrier mobility and highly ordered structure in the solid state. An additional feature of interest is represented by the possibility of preparing thin films with a suitable morphology by thermal evaporation under high vacuum conditions. These materials are mainly p-type semiconductors and the availability of n-type semiconducting compounds with the same structure opens the possibility of making bipolar transistors and complementary circuits in the perspective of novel organic-based electronics. Also in this case, attempts to convert the electronic characteristics of these materials were performed by introducing fluorine atoms or fluorinated alkyl groups onto the polynuclear aromatic system. A synthesis of perfluoropentacene **58** has been reported by Suzuki's group (Scheme 12).[54] The key steps are two Friedel–Crafts acylation reactions of tetrafluorophthalic anhydride with hydroquinone and quinone **56** derivatives. The substitution of oxygen atoms in the intermediate **57** was performed with HF/SF_4 and followed by Zn reduction leading to the final product **58**. In the solid state this compound adopts a herringbone structure, determined by X-ray diffraction of thin films obtained by high-vacuum sublimation in which the electronegative fluorine atoms overlap the electropositive pentacene moieties in the stacked layers. This type of arrangement should facilitate the charge transport, as previously discussed for the fluorinated thiophene or arylene oligomers. OFETs made using **58** work at 25–60 °C *in vacuo* and the high electron mobility (0.11 $cm^2 V^{-1} s^{-1}$) is comparable to the hole mobility of pentacene (0.45 $cm^2 V^{-1} s^{-1}$). A bilayer FET could be obtained by depositing pentacene over a layer of **58**. Actually, owing to the structural similarities of these two materials in the solid state, a continuous crystal growth occurs at the interface, as if a single material were used. A good electrical contact between the two layers allowed this device to work as an ambipolar FET, depending on the bias applied to the gate electrode. Moreover, FETs with pentacene and perfluoropentacene **58** were separately constructed on the same SiO_2/Si substrate, using appropriate masks, and interconnected in an inverter circuit configuration. These applications highlight the new perspectives for electronics based upon n-type organic materials.

Partially fluorinated pentacene **61** was obtained by the Cava reaction converting the α,α′-dibromo *o*-xylene **59** into the quinodimethane by *in situ* elimination of bromine with potassium iodide and reaction with 1,4-anthraquinone (Scheme 13).

The quinone derivative **60** was converted into **61** by reaction with tris(isopropyl)silylethynyllithium and reduction with tin(II)chloride. A rather similar procedure was used for preparing the octa-fluorinated diethynyl derivative **62** (Fig. 16).[55] The low-cost starting materials and the simple experimental procedure made it possible to obtain these derivatives in significant amounts, although the yields of some steps are not high. The single-crystal X-ray analysis of fluorinated pentacenes indicated a π-stacked arrangement with a strong interaction between the fluorinated and non-fluorinated rings, as previously pointed out for other fluoroaromatic systems. These strong interactions reduce the



Scheme 12



Scheme 13

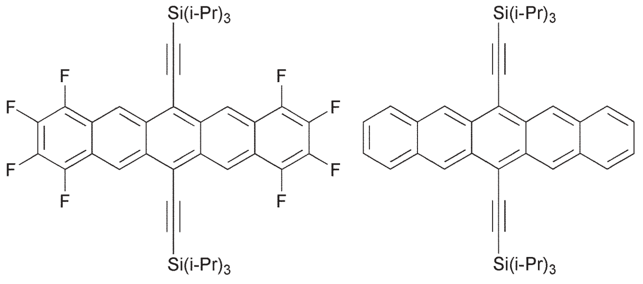


Fig. 16

interplanar spaces in the pentacene **62** with respect to the partially fluorinated **61** and the non-fluorinated pentacene **63**

The reduction of the spacing between the aromatic faces in the solid state may enhance the electron transport. The fluorinated pentacenes **61** and **62** have LUMO levels lower than the pentacene **63**, as observed from UV-vis and cyclic voltammetry data. This feature should confer an n-type semiconducting character to these materials. Actually, the pentacenes **61** and **62** are hole-transporting compounds as shown by measurement on FETs made by sublimation *in vacuo*. The hole charge mobility of these materials increases with the number of fluorine atoms (0.045, 0.014, and 0.001 $cm^2 V^{-1} s^{-1}$ for derivatives **62**, **61**, **63**, respectively). Thus the field-effect hole mobility scales with the π-face separation, which depends on the degree of fluorine substitution.

Although pentacene derivatives are characterized by high charge mobilities, they are scarcely soluble in organic solvents and rather difficult to synthesize. Anthracene can be more easily derivatized due to its better solubility. Therefore, the anthracene derivatives **64** and **65** (Fig. 17) were easily prepared *via* Stille or Suzuki–Miyaura cross-coupling reactions.[56]

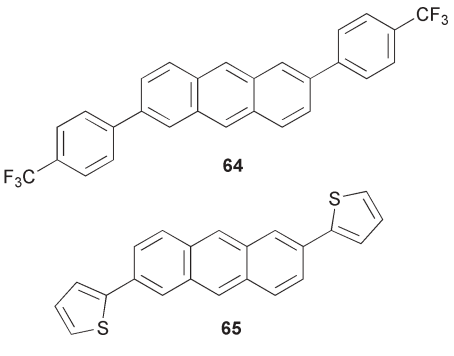
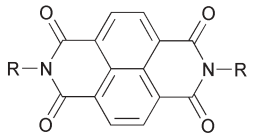


Fig. 17

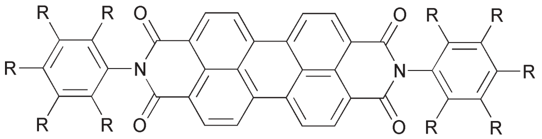
The insertion of trifluoromethyl groups is expected to confer n-type semiconducting characteristics to **64**, whereas the derivative **65** should behave as a p-type semiconductor. Both compounds are crystalline with a melting transition (DSC) at 289 and 322 °C, respectively. The single-crystal X-ray diffraction reveals a herringbone arrangement for the fluoro derivative **64**, showing the overlap of trifluoromethylphenyl rings with the anthracene nucleus, which, in turn, has some similarities with the solid state packing of the perfluoropentacene **58** reported above. The steric hindrance between the trifluoromethylphenyl ring and the anthracene nucleus forces **64** to adopt a twisted conformation (torsion angle 32.2°). On the contrary, the thienyl derivative **65** is nearly planar because of the reduced steric hindrance between the pentatomic rings and the anthracene unit. The X-ray diffraction of thin films obtained by high-vacuum sublimation of **64** on SiO_2/Si suggests an almost perpendicular disposition of the molecules on the substrate and this should be an ideal arrangement for charge transport. The same analysis for the thienyl derivative **65** evidences a disordered orientation. FETs made with the fluoro derivative **64** were operated *in vacuo* and showed a response only for positive bias, with an electron mobility of 3.4×10^{-3} $cm^2 V^{-1} s^{-1}$. The thienyl derivative **65** had the opposite behaviour with a hole mobility of 4.5×10^{-3} $cm^2 V^{-1} s^{-1}$. It is worth noting that the simple change of the aryl terminal groups in the anthracene moiety leads to materials with different polarities and similar mobilities.

Naphthalenetetracarboxylic acid diimides and perylene diimide are considered the most promising molecular materials with n-type semiconducting properties (Fig. 18).[57]

The simple *N*,*N′*-bis(octyl)-1,4,5,8-naphthalenetetracarboxylic diimide **66** works as an electron carrier in FETs under high vacuum with a charge carrier mobility of up to 0.16 $cm^2 V^{-1} s^{-1}$. However, the device is rapidly deactivated in air. The naphthalene diimide derivatives **67** and **68** have a semifluoroalkyl chain on the nitrogen atoms. They were synthesized starting from the naphthalene tetracarboxylic anhydride by high-temperature reaction with a suitable fluoroalkylamine. On the basis of single-crystal X-ray diffraction analysis, the molecules of **67** and **68** are packed in a dense, two-dimensional herringbone arrangement, similar to that of α-sexithiophene, generally associated with high carrier charge mobility. On the other hand, the solid state structure of the non-fluorinated derivative **66** is somewhat more disordered.



66 R = C_8H_{17}
67 R = $CH_2C_7F_{15}$
68 R = $CH_2C_3F_7$



69 R = F
70 R = H

Fig. 18

Thin films of the diimides **67** and **68** suitable for FET devices were obtained by solution casting at 30–100 °C, and electron mobilities in the range 0.01–0.06 $cm^2\ V^{-1}\ s^{-1}$ were measured in air. These materials are very appealing for OFET applications because of their suitability for thin film processing by simple casting from solvent, instead of the more expensive vacuum sublimation, and also because of the operativity of the devices in air. The great stability in air of the fluorinated materials with respect to the simple alkyl counterparts was attributed to the less negative reduction potential and to a more compact packing of the fluorinated chains, which makes these materials less permeable to water and oxygen.

The investigation of semiconducting properties of aromatic polynuclear diimides was also extended to more conjugated systems such as the *N*,*N*′-diperfluorophenyl-3,4,9,10-perylenetetracarboxylic diimide **69** and the related non-fluorinated counterpart **70**, obtained following the same procedure reported for the naphthalene diimides.[58] Also in this case the reduction potential of the fluoro derivative is less negative than that of the non-fluorinated counterpart, and this indicates that the reduced intermediate (a radical anion) of **69** is more stable due to the high π-conjugation of the perylene ring and the strong electron-withdrawing effect of the perfluorophenyl ring. The photoconductivity of both perylene derivatives **69** and **70** was measured in a blend with polyvinylcarbazole (PVK) at various monochromatic wavelengths. The much higher values for **69** clearly show that an easy electron transfer occurs from the electron donor PVK to **69**, resulting in a high exciton dissociation efficiency for the composite PVK/**69**. This good photoconductivity may be potentially exploited in organic solar cells. As in the case of naphthalene imides, the high solubility of **69** in common organic solvents allowed the fabrication of OFETs by a simple solution spin-coating process.[59] These devices are stable in air, but the electron mobility in the semiconductor is rather low (1.29×10^{-5} $cm^2\ V^{-1}\ s^{-1}$). This result may be ascribed to the semicrystalline morphology of the film.

(6) Organometallic iridium fluorinated complexes

Ir(III) phenylpyridine-based complexes are becoming increasingly important in applications such as light-emitting devices, due to their high quantum yields of luminescence and electroluminescence, stability and colour tunability.

The conversion of C–H bonds to C–F bonds may have several potential benefits:

(i) The C–H bond is a very effective promoter for radiationless decay of an excited state. Replacing the C–H bond with a C–F bond of lower vibrational frequency can reduce the rate of radiationless deactivation and enhance the photoluminescence efficiency.

(ii) In general, fluorination of the C–H bonds may make the compounds sublime better for thin film deposition.

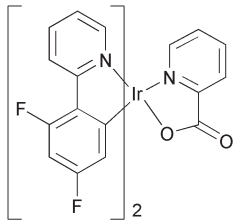
(iii) Introduction of a C–F bond or CF_3 group may alter the molecular packing and minimize the self-quenching behaviour.

(iv) Fluorination may sometimes enhance the electron mobility of the complex.

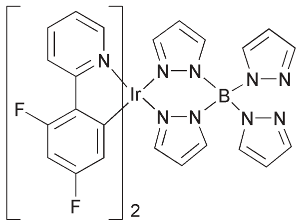
(v) HOMO and LUMO levels may be modified by fluorination, thus allowing the optimization of the carrier injection and the tuning of the electroluminescent colour. The most challenging and desirable colour remains the blue colour, due to the difficulties of designing and synthesizing complexes with a high energy emission, having, at the same time, high emission quantum yields and good stability for phosphorescent OLED (PHOLED) applications. Moreover, the synthesis of efficient "deep blue" light-emitters represents a very important step for the creation of white light-emitting devices (WOLEDs).

One of the best known triplet state blue light-emitters is iridium(III)bis(4,6-difluorophenylpyridinato-*N*,*C*$^{2'}$)picolinate (FIrpic)[60] **71** (Fig. 19), characterized by a reasonably good external quantum efficiency of about 10% in EL devices,[61] but its emission can be best classified as cyan in colour rather than blue.

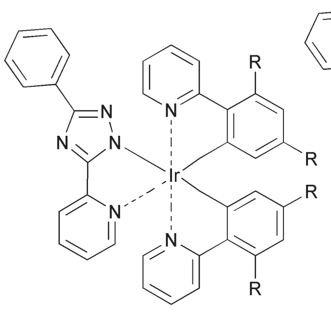
Another well known blue-emitting Ir complex for practical use is iridium(III) bis(4′,6′-difluorophenylpyridinato)-tetrakis-(1-pyrazolyl)borate **72** (Fig. 19) whose blue OLED, obtained



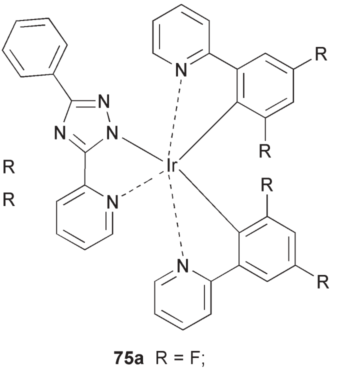
71 FIrpic



72



73 R = H;
74a R = F;
74b R = CF_3;



75a R = F;
75b R = CF_3;

Fig. 19

by doping the complex in suitably wide energy gap hosts, showed an external quantum efficiency of 9–10% (λ_{max} = 457 nm) and whose blue colour chromaticity is considerably improved with respect to FIrpic.[62]

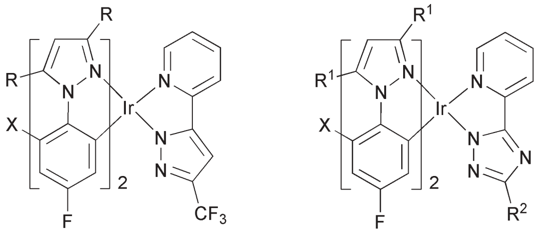
Besides these most commonly investigated materials, the search for blue-emitting Ir complexes is a very active field and various structures have been proposed.

De Cola and co-workers reported a room-temperature procedure for the preparation of various heteroleptic fluorinated green-blue-emitting complexes based on new phenylpyridines carrying fluorine atoms or trifluoromethyl groups and triazolyl pyridines as the ancillary ligands (Fig. 19). A study of the emission spectra showed the effects of fluorine and trifluoromethyl groups in different positions of the phenylpyridine ligands on the emission properties.[63]

The complex **75a** shows a negligible blue-shift in the emission (λ_{max} = 484 nm) when compared with the non-fluorinated analogue **73** (λ_{max} = 489 nm), while the complex **74a** shows a hypsochromic shift of about 28 nm resulting in an almost blue emission (λ_{max} = 461 nm). The difference in behaviour was attributed to the double nature of the electronic effect of the fluorine atom, which is inductive and mesomeric. In fact, the *meta* position on the phenyl ring in complex **74a** with respect to fluorine atoms is the most electron-deficient because it is affected only by the inductive electron-withdrawing character of the fluorine atom. As a consequence, the σ-donation from the cyclometalating ligand to the iridium ion is reduced and the ^{3}MLCT (metal-to-ligand charge transfer state) emitting level is raised. Contrary to this, in the case of complex **75a**, the coordinating carbon is less electron-deficient because the electron-withdrawing effect of the fluorine atom is compensated for by its electron-donating mesomeric character. The combination of the two factors causes only a negligible effect on the spectroscopic properties of complex **75a** compared with the unsubstituted complex **73**. It is not surprising that the trifluoromethyl group shows an opposite behaviour: when CF_3 groups are in *ortho*- and *para*-positions with respect to the metal centre (**75b**), there is a strong blue-shift (λ_{max} = 466 nm) with respect to the unsubstituted complex **73**, indicating these positions as the most effective in tuning the emission towards the blue region. In contrast, the complex **74b** bearing the CF_3 groups in the *meta*-position with respect to the coordinating carbon shows a bathochromic shift in the emission maximum of 22 nm (λ_{max} = 511 nm) when compared with **73**.

In a series of heteroleptic Ir(III) complexes bearing 2-pyridyl pyrazole (or triazole) (Fig. 20) as the ancillary ligand, the insertion of fluorine atoms or perfluoroalkyl chains leads to blue emission with peak wavelenghts at 450–470 nm in dichloromethane solution.[64] All of the complexes exhibit a very good photostability but quite low quantum yields in degassed dichloromethane solution, which are only slightly dependent on pendant substituents such as Me, CF_3 or C_3F_7.

In comparison with the behaviour in solution, these materials have an increased quantum yield in the solid state. In particular, for complex **76a** the quantum efficiency was 0.13, while that of the other complexes was still too low. No device is reported for these complexes, even if their colour appears promising for blue-emitting devices.



76a X = F, R = H
76b X = H, R = H
76c X = F, R = Me
76d X = H, R = Me

77a X = F, R^1 = H, R^2 = CF_3
77b X = H R^1 = Me, R^2 = CF_3
77c X = F, R^1 = H, R^2 = C_3F_7
77d X = H, R^1 = H, R^2 = C_3F_7
77e X = F, R^1 = Me, R^2 = C_3F_7
77f X = H, R^1 = Me, R^2 = C_3F_7

Fig. 20

The pentafluorophenyl group bound to various positions of the phenylpyridine ligands in Ir heteroleptic complexes was reported to tune both photoluminescence and electroluminescence spectra to either shorter or longer wavelengths by changing the energy levels of the triplet metal-to-ligand charge transfer emitting state.[65] The pentafluorophenyl ring was found to red-shift the emission of complexes **78b**, **78c**, **78d** and to blue-shift the emission of **78a**, with respect to the corresponding non-functionalized heteroleptic complex (Fig. 21).

On the whole, the peaks of the electroluminescence spectra were tuned from 513 to 578 nm (colour ranging from green to orange), with external quantum efficiencies ranging from 10 to 17%.

The effects of fluorine atoms on the photophysics of homoleptic complexes were also evaluated by various groups.

Blue-shift in homoleptic Ir complex emission induced by the introduction of fluorine atoms on ligands was observed by

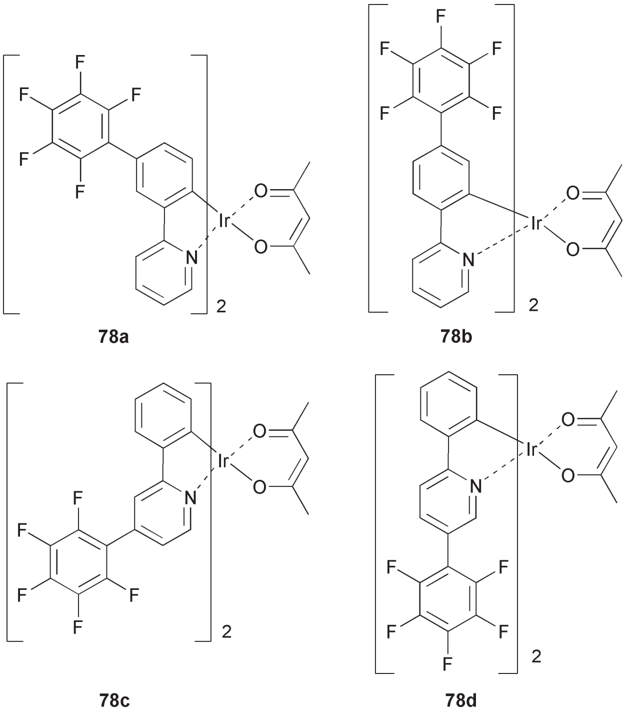


Fig. 21

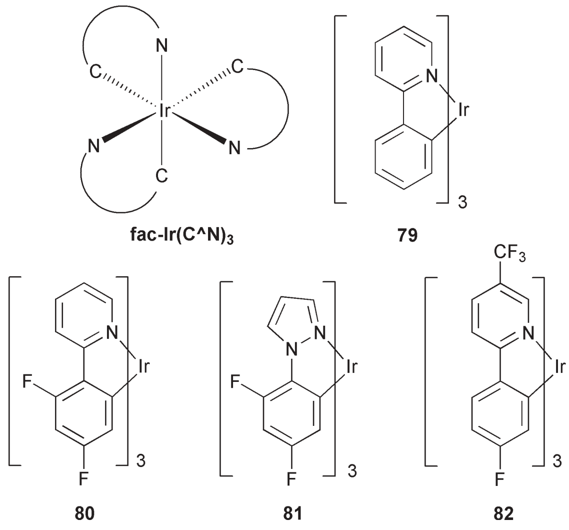


Fig. 22

Thompson and co-workers.[66] Comparing the *fac*-tris(phenylpyridine) complex **79** with the corresponding complex **80** (Fig. 22), the blue-shifted emission (λ_{max} = 492 nm *vs.* λ_{max} = 450 nm, respectively), already observed in Pt(II) complexes,[67] was attributed to the electron-withdrawing fluorine atoms which stabilize the HOMO more than the LUMO level, thus increasing the triplet energy gap. Addition of electron-withdrawing fluorine atoms on the phenyl ring of the phenylpyrazolyl ligands also blue-shifts the emission of the corresponding *fac* homoleptic cyclometalated complex **81**, so that its triplet energy falls in the ultraviolet region (λ_{max} = 390 nm).

Wang *et al.* reported a fluorine- and trifluoromethyl-substituted Ir complex **82**[68] and, also in this case, a strong influence of the fluorinated substituents on the properties of the materials could be observed. Thermogravimetric analysis showed that the sublimation temperature of the *fac* complex **82** is about 70 °C lower than that of **79**, as expected because of the effect of fluorination. The photoluminescence quantum yields of **82** in the solid state was 10 × that of **79**. Since the molecular photoluminescence values of **79** and **82** measured in dilute solution are similar, the dramatic difference observed in the solid state could be attributed to changes in the intermolecular interactions dictated by the different intermolecular packing. A unique feature of the complex described by Wang *et al.* is that it could be used as emitting active layer in a PHOLED device in the undiluted form, without the use of a charge-transporting host, due to its good charge-transporting properties. The electron-transporting properties appear to be enhanced by fluorination and the barrier to electron injection reduced, as indicated by the lower LUMO energy, which results in a more balanced electron–hole recombination in the luminescent layer. Actually, the LED peak efficiencies of fluorinated complex **82** and the non-fluorinated complex **79** were 20 and 3.8 cd A^{-1} respectively in an LED configuration involving the hole-transporting bis[4-(*N*,*N*′-dimethylamino)-2-methylphenyl](4-methylphenyl)methane (MPMP), the electron-transporting 4,7-diphenyl-1,10-phenantroline (DPA) and an Al cathode.

The high efficiency of the brilliant green electroluminescence (maximum of emission at 525 nm) observed for **82** is a result of the combination of the ability to transport both electrons and holes and of the strong reduction of luminescent self-quenching in the solid state.

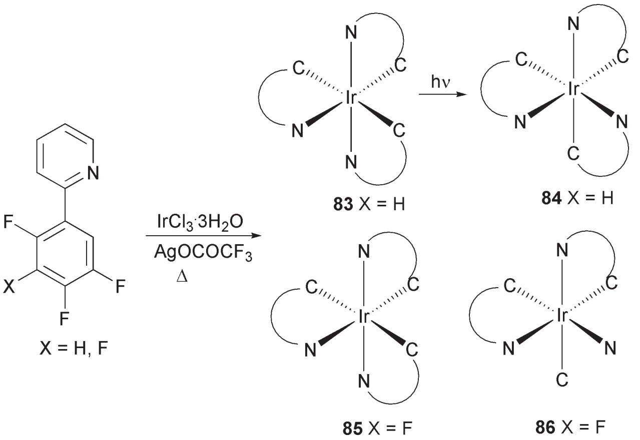
Recently, we have reported the synthesis and characterization of a series of homoleptic and acetylacetonate heteroleptic iridium complexes bearing three or four fluorine atoms directly bound to the phenyl ring of the phenylpyridine ligands in order to decrease the HOMO energy and, as a consequence of the increased HOMO–LUMO energy gap, to obtain blue-emitting phosphorescent complexes.[69]

Fluorinated phenylpyridine cyclometalating ligands were obtained *via* the Stille cross-coupling reaction.

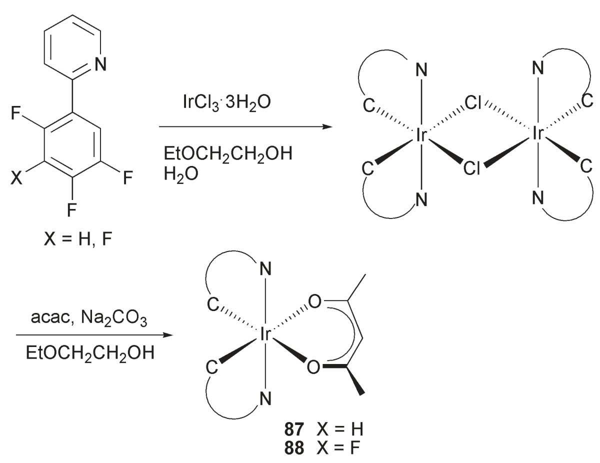
The homoleptic complexes were synthesized in a single-step procedure, previously reported,[70] involving the reaction of $IrCl_3 \cdot 3H_2O$ with a slight excess of fluorinated phenylpyridine ligand, in the presence of silver trifluoroacetate (Scheme 14). At variance with the results reported in the literature, where only the *facial* stereoisomers were obtained by this approach, in our case, when the tetrafluoro-substituted ligand was used, it was possible to obtain both the *meridional* and the *facial* stereoisomers depending on the reaction temperature. In the case of the trifluoro-substituted ligand, the complexation reaction afforded only the *mer* isomer and a photochemical isomerization process was necessary to synthesize the corresponding *fac* isomer (Scheme 14).

Heteroleptic acetylacetonate complexes were obtained by the preliminary synthesis of the corresponding dichloro-bridged dimeric complexes followed by reaction of these intermediates with the anionic ancillary ligand acetylacetonate (Scheme 15).

All of the fluorinated complexes obtained exhibit broad emission in the "light blue" region, and the emission spectra appear significantly affected by the number of fluorine atoms bound to the phenyl rings of the ligands. Actually, under the same stereochemical configuration, the emission is 10 nm blue-shifted for complexes bearing three fluorine atoms on each phenylpyridine ligand with respect to the corresponding complexes bearing a further fluorine substituent in the 5′-positions of the ligands. The replacement of one of the three phenylpyridine ligands with acetylacetonate (Scheme 15)



Scheme 14



Scheme 15

shifts the emission of complexes bathochromically by about 10 nm regardless of the number of fluorine atoms. The *fac* and *mer* stereoisomers of the homoleptic Ir complexes have different wavelengths of the emission maxima at room temperature. Furthermore, the complexes **83** and **85** are blue-shifted by 5 and 4 nm, respectively, in comparison with the corresponding *fac* isomers **84** and **86**. Electroluminescent devices were fabricated using the Ir complexes dispersed (9% concentration) in a poly(9-vinylcarbazole) (PVK) host matrix in the presence of an electron carrier molecular material and a hole-blocking layer. All of the complexes emitted with potentials between 5.0 and 6.5 V, showing emission maxima in the blue region and shapes and energies similar to those found in solution emission. The maximum external quantum efficiency (5.5%) was observed for the device made with complex **86**. Furthermore, electroluminescence experiments showed a critical difference in the stability of the devices fabricated with the *fac* and the *mer* isomers. In fact, the device with the *mer* complexes exhibits a fast spectral change of the emission from the blue to the green region of the spectrum. The devices made with the heteroleptic complexes showed reduced efficiencies with respect to the homoleptic *fac* complexes (2.2% for **87** and 3.2% for **88**, respectively).

Conclusions

This contribution briefly reviews the features of fluorinated conjugated materials with semiconducting properties for applications in some organic-based electronic devices such as OLEDs and OFETs. Many methodologies are available for the synthesis of these compounds, but organometallic processes such as the Stille or Suzuki–Miyaura cross-coupling reactions appear the most versatile synthetic pathways.[4] The presence of fluorine atoms or fluorinated alkyl or aryl sustituents interacting with the main π-conjugated system of these materials substantially induces a significant lowering of the HOMO and LUMO energy levels with respect to the non-fluorinated counterparts. A low-lying LUMO level implies a facilitated electron injection. A better energy match between the LUMO level in fluorinated PPVs and a relatively high work function metal such as aluminium avoids the use of less durable calcium or barium for the cathode electrodes in OLEDs. Moreover, an improved hole–electron balance in charge injection enhances the efficiency of the devices. Homoleptic and heteroleptic iridium complexes with the proper fluorine substituents have been used as effective phosphorescent blue-emitters in recent PHOLED technology.

Fluorinated oligothiophenes, phenylene-thienylene oligomers and polynuclear aromatic compounds (pentacenes, anthracenes and perylenes) represent very promising materials with n-type semiconducting properties, also induced by the LUMO lowering effect of fluorine atoms. Moreover, highly ordered π-stacking of these materials in the solid state enhances the charge carrier mobilities, which is an essential feature for OFET applications.

The lowering of the HOMO level makes fluorinated conjugated materials less susceptible to oxidative degradation and, therefore, the replacement of C–H bonds with the stronger C–F bond has some effects upon the device lifetimes made with fluorinated organic semiconductors. However, up to now, it does not seem that this point has been investigated as deeply as it would deserve and further studies are needed.

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