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Chapter 1

ELECTRODE COATINGS CONSISTING OF POLYTHIOPHENE-BASED COMPOSITES CONTAINING METAL CENTRES

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ABSTRACT

Polythiophene derivatives constitute nowadays the most extensively studied class of conducting polymers, thanks to their mechanical and thermal stability, as well as to their physical and chemical properties, such as electronic conductivity, electrochromism, solvatochromism, thermochromism and luminescence. These materials have been proposed for use in a wide range of applications, including chemical sensors, light emitting diodes, thin film transistors, different electrocatalytic systems, batteries, smart windows, and even artificial muscles.

Peculiar systems are realised by anchoring similar materials on substrates. In particular, conductive substrates suitably coated by polythiophene derivatives constitute particularly interesting electrode systems that can be exploited in numerous electrochemical-electroanalytical applications. However, a notable part of the research activity in these fields is today evolving toward the insertion of metals into the polythiophenes matrix, in order to further improve the performances of the pure organic material. The driving force to these studies lies in the possibility to combine the properties of the organic and inorganic entities, taking advantage of their synergic interaction. Basically, two different approaches, resulting in hybrids/composites of quite different nature, have been followed: i) *link* of metal complexes to the polymeric backbone; ii) *inclusion* of metal ions and complexes, of clusters, oxides or nanoparticles into the polymer. In similar systems, the presence of the metal is supposed to deeply affect the electronic and electrochemical properties of the resulting hybrid/composite material.

The aim of the present contribution is to give a picture of the variety of polythiophene-based hybrid/composite materials developed, with reference to the systems in which the polymer is supported on a conductive substrate, to constitute an electrode system. The different physico-chemical characterisations are treated, mainly

devoted to clarify the interactions between the polymer and the metal centres, as well as the nature of the interface between the ambient and the composite as a whole. Description is given of some applications in electrochemical environments.

1. INTRODUCTION

After more than 20 years of increasing interest, conducting polymers (CPs) are nowadays acknowledged to constitute an extraordinarily important class of materials, offering a particularly wide range of innovative applications [1-8]. CPs constitute a class of molecules containing a conjugated π -electron system that confers the material unusual electronic and optical properties, such as high electrical conductivity, low ionisation potential and high electronic affinity, as well as low-energy optical transitions. Furthermore, one of the most interesting characteristics of CPs lies in the possibility to be 'switched' forth and back to/from highly conductive states. This switch involves partial oxidation and partial reduction of a neutral electronically semiconductive parent polymer backbone to form a polycationic or polyanionic chain, respectively. The corresponding so-called *p*- and *n*-doping processes are induced either chemically or electrochemically. The first step of oxidative doping lies in the formation of a radical cation (*polaron*) (see Figure 1), inducing localised geometrical distortion along the polymer chain. The de-localisation of similar charge defects over several units constitutes one of the mechanisms at the basis of the conduction of doped CPs [2,9]. With increasing the doping level, one additional charge is removed from a reduced enough portion of the chain; as a result of the strong electron-lattice interaction, two radical cations coalesce into a dication (*bipolaron*), which is a doubly charged spinless deformation on a π -conjugated chain. The polymer reductive doping occurs in a similar way, the doping process rendering the polymer chains negatively charged. In both doping states, the overall electroneutrality of the resulting material is preserved by the incorporation of counterions from the solution. Figure 2 reflects what described from a mechanistic point of view into an energy diagram. The energy difference between valence and conducting bands is a measure of the *band-gap* and determines the intrinsic properties of the material: CPs possessing a particularly low band-gap value, i.e., lower than 2.0 eV, can easily become conductive either for oxidation or for reduction, consequently opening to a number of possible applications of the material. The band-gap can be estimated from the difference between the *p*- and *n*-doping potential values.

The conduction process inside a CP is quite complicated [2,9]. It not only involves charge delocalisation along single polymer chains (*intra-chain* conduction), but it is also based on mechanisms of charge transfer from one chain to another (*inter-chains* conduction) and between different segments of the same chains. Many experimental results indicate that the inter-chain transfer is the rate-limiting step. For this reason, many works, also reported in the present chapter, are finalised to improve the inter-chain conduction, mainly by bridging different polymer chains through the formation of proper chemical bonds.

In principle, a number of new functional polymers can be synthesised, starting from suitable monomers possessing π -electron conjugation. The most extensively studied and widely applied CPs are polypyridines, polypyrroles, polythiophenes, and even polyfurans and carbazoles. The properties of numerous copolymers have also been studied. Among the different CPs, *polythiophene* (PTh) derivatives constitute a particularly important class of

materials, thanks to properties such as the cited electrical conductivity, as well as electrochromism, solvatochromism, thermochromism, luminescence, etc.[1,10,11]. Compared with other π -conjugated polymers, the properties of PTh can be deeply modified by inserting a number of different substituents in β and β' position. This possibility has stimulated the realisation of many different PTh derivatives possessing a wide range of physico-chemical properties. In particular, long-chain alkyl substituents or, on the opposite side, ionic residues, have been inserted in order to favour solubility in apolar [12] or in polar [13] solvents, respectively; good solubility constitutes an essential property for most applications of these materials, especially when they have to be filmed on surfaces through drop casting or spin coating. On the other hand, electron-donating groups, such as alkoxy or alkylsulphonyl chains, have been inserted to significantly decrease the p-doping potential and, as a consequence, the band-gap [10,12,14]. Finally, specific functional groups, such as crown ethers [15,16] and calixarenes [17], have been bonded to the PTh backbone, in order to allow selective interaction with species present in solution.

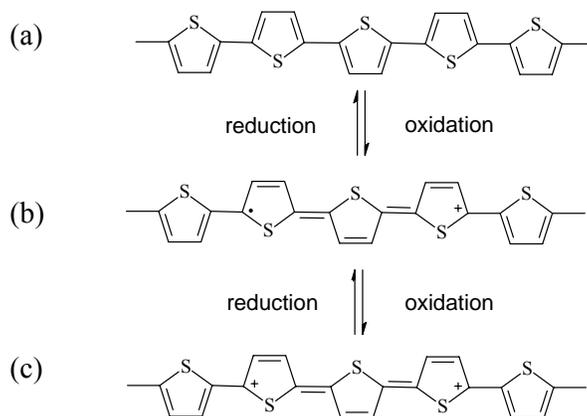


Figure 1. Schematic structures of (a) neutral, (b) positive polaron and (c) positive bipolaron states in a polythiophene chain.

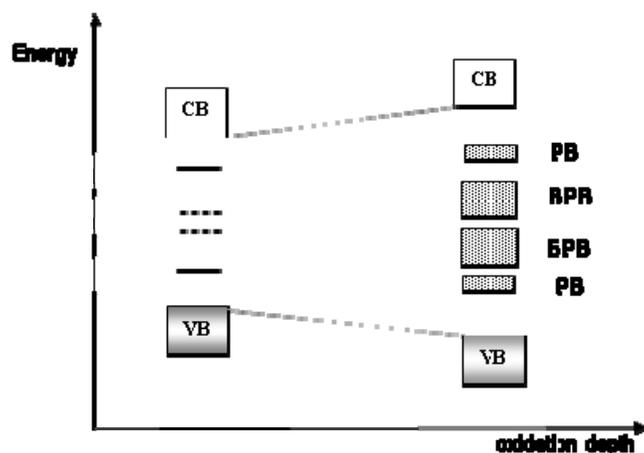


Figure 2. Evolution of the CP energy bands during oxidation: VB: valence band; CB: conducting band; PB: polaron band; BPB: bipolaron band

PTh derivatives have been proposed for a wide range of applications, including chemical sensors, electroluminescent devices, electrocatalytic systems, batteries and capacitors, smart windows, artificial muscles and memory devices [18]. Within this list, the development of electrode coatings for sensoristics constitutes one of the most attractive fields of research [11,12,15,18]. In particular, the advantages of similar modified electrodes as amperometric sensors, with respect to the conventional bare metals and even to alternative coatings, are ascribed to anti-fouling and electrocatalytic properties, concurring to provide the systems for excellent repeatability of the responses obtained, for high sensitivity, low detection limit and even, thanks to suitable substituents, for possible selectivity [15,19-23]. The most spontaneous way to realise electrodes modified with similar coatings is to polymerise the thiophene-based monomer by electrochemical oxidation. Although the definition of the relevant mechanism still constitutes a debated item, the reaction path generally accepted consists of electrochemical (E) and chemical (C) steps [24], as outlined in Figure 3. Once the length of the growing chains has reached such a value that they are not soluble anymore, a portion of the polymer deposits onto the electrode surface. It has to be underlined that the polymer chains formed during the electrogeneration process are positively charged; thus, the last step of the film deposition may consist in the neutralisation (de-doping) of the film through application of a suitable potential.

A key point to obtain a material with the desired properties consists in a polymerisation occurring at fairly low potentials. This also in order to avoid possible polymer overoxidation that irreversibly modifies the material, lowering or even cancelling its conductive character. Just thanks to easy oxidation, thiophene derivatives bearing in the β -positions different alkyl chains or, even better, stronger electron-donating substituents, are often preferred. With this respect, 3-methylthiophene (3MT) shows a markedly lower oxidation potential value with respect to unsubstituted thiophene (Th); for this reason it has been the object of many researches for possible applications of the relevant polymer (P3MT) in many different fields, amperometric sensors included.

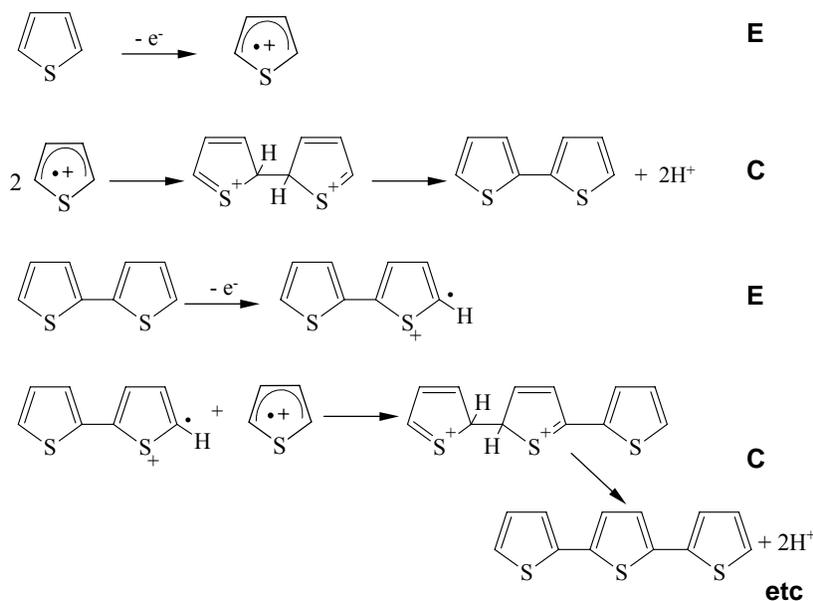


Figure 3. Proposed mechanism for electrode polymerisation of thiophene

Nowadays, one of the most widely used Th derivatives is 3,4-ethylenedioxythiophene (EDOT), also thanks to its fairly high solubility in aqueous media. This monomer shows very low oxidation-polymerisation potential, ascribed to the strong electron-releasing effect of the ethylenedioxy group. This aspect also imparts peculiar properties to the relevant polymer (PEDOT), which shows quite high conductivity and stability, and a particularly low band-gap value [25,26]. The potentiality of this polymer in a very wide range of applications is also increased by the possibility to synthesise water soluble materials based on this polymer; in this case, polymerisation of EDOT is carried out in the presence of a water soluble polyelectrolyte, such as sodium polystyrene sulphonate (NaPSS) [27].

Due to delocalisation of the positive charge arising from oxidation, bi- and ter-thiophene derivatives constitute interesting starting monomers for the obtainment of the corresponding polymers at low applied potentials. The choice of dimers or trimers as starting species is particularly profitable, or even mandatory, when bulky substituents are present on the PTh chain, since steric hindrance may prevent coupling of the single-ring monomers.

Recently proposed materials with the properties sought, with respect to modification of the pristine PTh chain, consists in developing multifunctional materials in which the polymer acts as a stable and conductive component to combine with other entities. The resulting class of materials originates from more or less organised 'combination' of two or more nanosized components, resulting in unique physical properties, usually different from those inferable by a simple 'sum' of the ones proper for the starting materials. Of course, the PTh matrix possesses on its own typical properties; if it is even functionalised, the term 'multifunctional material' is more and more enforced. In particular, the inclusion within PTh of inorganic species, under the form of metal ions, of metal clusters or of metal nanoparticles, represents an opportunity for the design of materials with improved properties, such as higher conductivity, increased electrocatalytic properties and enhanced energy storage capabilities [19,28-34]. The resulting materials are often defined either as hybrids or as (nano)composites. Even if there is no clear border between these two different kinds of materials, the term *composite* is generally given to materials made by different components, well distinct from each other on a macroscopic level, while the term *hybrid* generally refers to materials that include different moieties blended on the molecular scale [35]. In the present contribution, we aim at reviewing different kinds of hybrid/composite PTh-based materials containing metals under whatever form, focusing on the possible improvement of given properties with respect to the pure organic component. This survey also reports an illustration of the different techniques employed for a complete characterisation of the hybrid/composite materials and also points to selected applications.

2. METAL IONS COVALENTLY BONDED TO POLYTHIOPHENE BACKBONE

One of the most promising way to improve the performances of PTh derivatives lies in the introduction of redox metal centres bonded to the polymer backbone by a substituent bearing a metal ligand [15,33,34,36-42]. The impulse to develop similar hybrid materials comes from the possibility to combine the well known chemical, optical and electrochemical properties of PTh derivatives with those of metal complexes, taking advantage of the

interaction between the organic and inorganic frames. Similar materials, most widely investigated since the beginning of the nineties, are generally referred to as *metallopolymers*. A number of chemical structures has been proposed in the literature, showing different reciprocal disposition of metal ions and organic backbone, as outlined in Figure 4.

Most properties of the resulting material are related to the nature of the charge transfer through the hybrid material, i.e. occurring by either electronic or *electron hopping* mechanisms. This process is strongly affected by the material as a whole, i.e. by the nature of the metal and of the organic ligand, as well as by the connection between the ligand and the polymer π -backbone. With this respect, many studies have been specifically devoted to clarify the nature of the electronic interaction between metal and polymer and between different metal ions inside the film, especially by electrochemical, spectroelectrochemical and *in situ* conductimetric investigations. Exhaustive critical examinations of these aspects are found in some recent reviews [33,34,43].

Considering the wide number of materials proposed in recent years, the different metallopolymers can be roughly, though conveniently, divided into two main categories [34,38]. In a first one, the metal centre is far from the polymer backbone, separated by a relatively long non-conducting spacer, typically by an alkyl chain (Type I in Figure 4). A similar structure results particularly profitable when inserting bulky substituents, which can induce distortion of the π -conjugated system, with consequent adverse effects upon important PTh properties, such as the intra-chain conductivity. Similar materials are characterised by the absence of significant electronic interaction between the metal and the polymer π -backbone. In this case, the charge transfer between two neighbouring metal centres occurs by electron-hopping, also called outer-sphere mechanism [2,6], while an electronic conduction is operative along the organic chain. Since such a situation is characterised by the absence of any overlaps of the metal d-orbitals to the polymer π -orbitals, the properties of the material are merely the sum of those of the metal complex and of the polymer backbone. The advantages of developing a material within this class reside in the possibility to stably fix redox centres inside a conductive matrix, also improving the charge transfer efficiency through the film, in particular from one metal centre to another. With this respect, similar materials represent a definite step forward with respect to redox polymers, i.e. insulating polymeric chains bearing metal redox centres.

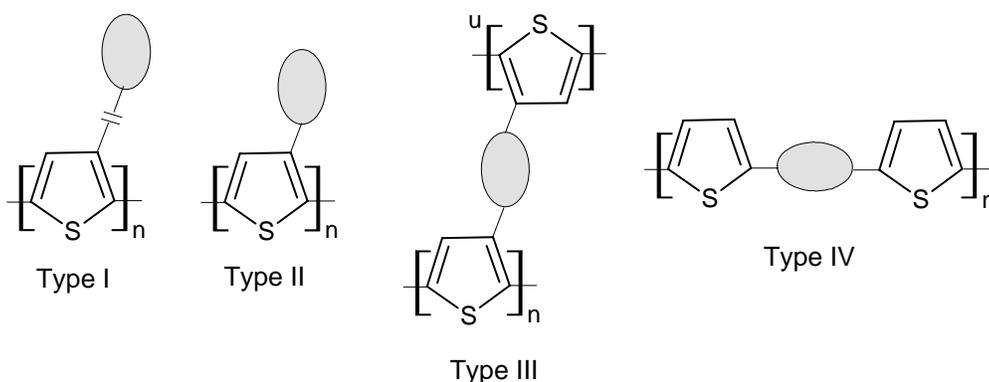


Figure 4. Schematic representation of different varieties of metallopolymers, classified on the basis of the reciprocal position of Th chain and metal complex.

In the opposite situation, the metal ions can be close enough to the polymer backbone to strongly interact with the π -system responsible for the electronic conductivity of the polymer. When the energies of the metal d-orbitals and of the π -conjugated polymer system are close to each other, the charge transport along a metallopolymer chain occurs through an inner sphere mechanism: the communication between the metal centres may be mediated by the polymer backbone and, in turn, the charge delocalisation along the chain involves the electrons of the metal to some extent. In this case, the resulting material shows peculiar properties, often quite different from those that could be deduced from the characteristics of the individual organic and inorganic entities. Within this class of metallopolymers, different sub-classes can be identified. In particular, the metal complex can be either located on a lateral chain electronically connected to the PTh π -backbone (Type II and III in Figure 4), or even positioned within the π -backbone (Type IV in Figure 4). Correspondingly, β - or α -functionalised (oligo)thiophenes are employed, respectively. It should be underlined that the choice to introduce the metal ligand in the α -position of the Th ring strongly limits the length of the π -conjugation and, consequently, the potential at which the material is doped may result rather high. In any metal-Th configurations above described, the metal ions can also act as the cross linkers between two adjacent polymer chains, as in Type III in Figure 4. In this case, the efficiency of the inter-chain charge transfer results significantly improved with respect to pure polymeric materials [44].

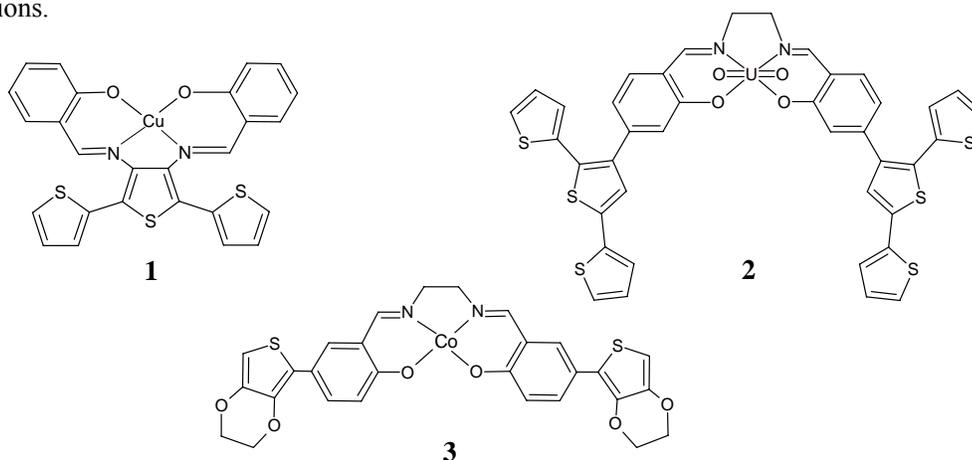
Two synthetic approaches to the development of similar hybrid materials have been reported. In a first one, a PTh functionalised by the suitable metal ligand is obtained by a first synthetic step; in a following step metal ions are introduced by simply dipping the modified electrode into a solution containing the suitable salt. Such an approach has been only rarely employed [45-52], since the fraction of actually complexed ligands can not be easily evaluated at the end of the procedure. On the other hand, it is quite advantageous in order to investigate the effect of the presence of the metal on the properties of the whole material, on the basis of a comparison between the behaviour of the uncomplexed and the complexed polymer, i.e. before and after the dipping step, respectively [46,51]. In a different, merely analytical context, the development of similar pure organic polymers, capable to 'capture' metals by complexation, has shown to be effective in the detection of metal ions that selectively interact with the ligand bonded to the polymer chain [15,36].

A more extensively explored and adopted approach consists in the polymerisation of a monomer in which the ligand moiety has been previously complexed by the metal. In the most part of the reported examples, an electrochemical oxidative polymerisation process is used for the formation of the relevant metallopolymer. The metal ions that are most profitably introduced in these materials are suitable to be reversibly oxidised and/or reduced in the potential interval where the organic polymer is stable. In particular, the list includes [33,34] Co, Ni, Cu, Fe, Ru, Os but also, even if less extensively explored, Rh, Au, Pt and Pd. Oxidation states that are poorly stable in the solution phase may be expected to possibly acquire higher stability in such a chemical environment, allowing interesting and even new electrocatalytic processes to be envisioned.

Many metallopolymer derivatives contain nitrogen-based ligands [33,34]. Similar ligands are capable to strongly coordinate a variety of metals, so that it is even possible to compare the properties of hybrids differing as to the metal. In particular, *salen*-type derivatives, such as compounds 1, 2 and 3, reported as examples, have been widely explored, also due to the

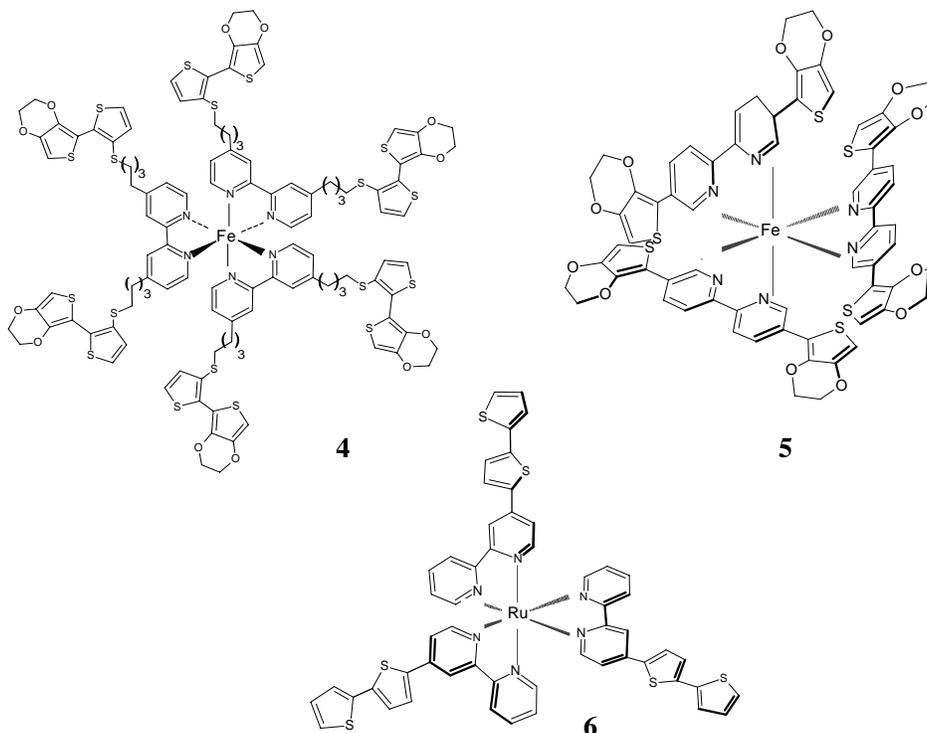
simple syntheses involved and to the stability of the relevant complexes, which prevents from de-complexation under a broad range of conditions. By exploiting the β and β' positions of the Th ring to link the ligand, as it happens in compounds 1 and 2, the α and α' positions are free to link two additional Th rings, which is a necessary condition to reduce the steric hindrance due to the presence of salen, as well as to lower the polymerisation potential of the monomer [53-58]. In a different, more recent approach, the salen ligand is in the α - position of a Th unit capable to act as the active moiety in the polymerisation, as it is verified in compound 3, taken as a representative example [59-66]. In this case, the use of EDOT outer rings is advantageous in order to obtain coincidence of the oxidation potential of the polymer with that of the salen-based metal complex, which further enhances the conductivity of the material [59-61,63,64]. Moreover, when ligands containing two differently substituted Th outer rings are used [65,66], it was demonstrated that the polymerisation is significantly improved by the presence of metal ions coordinated to the salen moiety; such an effect is ascribed to a charge propagation along the Th–salen units, mediated by the metal.

As a final consideration regarding this class of materials, recent studies have focused on the effect induced by the insertion of different kinds of diamine bridges [60,64-66]. On the one hand, the introduction of bulky functional groups, such as 1,2-diphenylethylenediamine and *cis*- or *trans*-1,2-diaminocyclohexane, significantly increases the inter-chain spacing inside the polymer film, preventing from π -stacking between polymer chains. This effect results in a lower conductivity of the material with respect to a similar polymer film containing simple ethane diamine bridges [60]. In a different context [64], the introduction of a neopentyl linker enhances the solubility of the monomer and increases the flexibility of the ligand at the same time, favouring the expansion of the coordination sphere of the metal when interacting with the analyte. Finally, chiral substituents were introduced [65,66] in metallopolymers with catalytic properties, in order to activate asymmetric condensation reactions.



2,2'-bipyridine is one of the most frequently encountered nitrogen-based ligands in metallopolymers [43,44,67-80], also due to the well known luminescence properties of $[\text{Ru}(2,2'\text{-bipyridine})_2]^{3+}$ complexes, possibly enhanced by the link to an electronically delocalised π -system. For this reason, many of the reported examples of similar metallopolymers regard Ru(II) [44,67,68,70-79]; Os(II) [72,80] and Re(I) [70] have been also considered for studying similar phenomenon. Bipyridine-based complexes also show

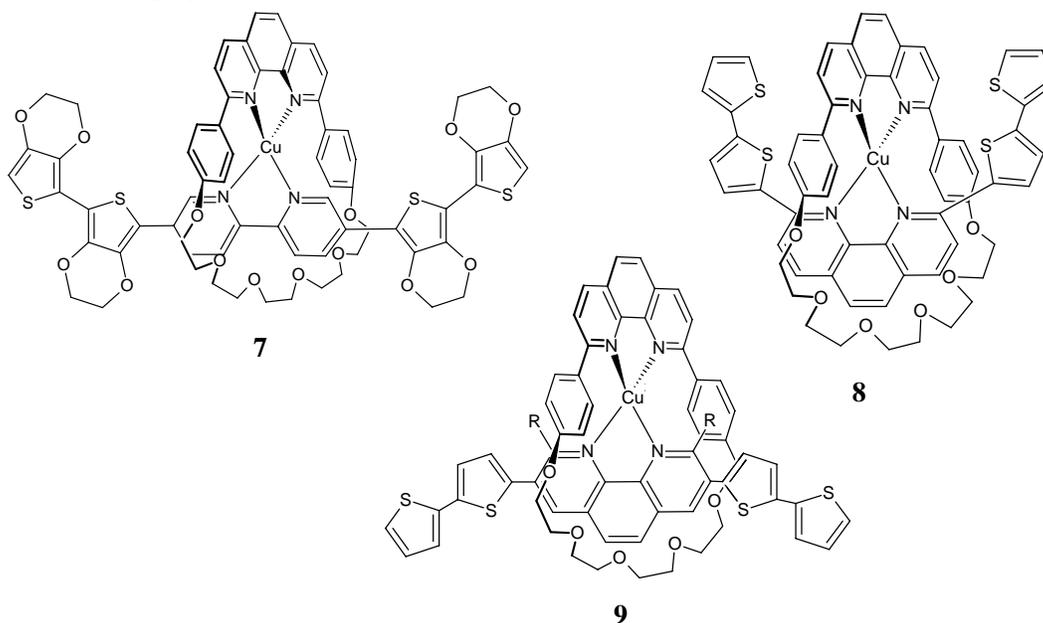
reversible redox behaviour, which suggests useful applications in the field of electrocatalysis; for this reason, Fe(II) [46,69,74,77], Co(II) [46,74], Ni(II) [46,74] and Cu(II) [46] bipyridine complexes have also been studied. With this respect, many different kinds of bipyridine-(oligo)thiophene derivatives have been synthesised, in order to obtain the relevant metallopolymers with the properties sought; compounds 4-6 constitute three representative examples. Several authors synthesised monomers in which bipyridine is connected to the Th ring in one of the β positions through an alkyl chain of different length [68-70]; electropolymerisation of these derivatives results, in general, rather difficult and does not lead to very stable deposits. In order to overcome these problems, Roncali et al. [77] synthesised three new derivatives characterised by 2,2'-bipyridine moieties bearing two bithiophene rings at a β -position, as compound 4 illustrates. Different authors preferred directly bridging the bipyridine moiety between two Th or oligothiophene derivatives at the α -positions [44,46,67,71-76,78-80], similarly to compound 5. Even if the major number of similar derivatives involves 5,5'-substituted bipyridine [46,67,71-74,76,77], Swager et al. [44] found that they are characterised by only limited interaction between neighbouring metal centres, as a result of the lack of effective electronic conjugation between the oligothiophene chain and the metal binding sites. On the contrary, 4,4'-substituted 2,2'-bipyridine derivatives generate a metallopolymers in which neighbouring metal centres effectively communicate through π -orbitals of the conjugated bridge. A further possibility consists in the synthesis of bipyridine derivatives where only one of the two pyridine rings is bounded to a (oligo)thiophene ring [44,75] (see compound 6); the relevant metallopolymers are characterised by a reduced cross-linking with respect to the corresponding bi-substituted bipyridine derivatives [44]. The comparison between the two materials demonstrates that a cross-linked polymer network facilitates the conduction inside the whole material.



Further considerations regarding bipyridine-based metallopolymers concern the number of bipyridine-(oligo)thiophene ligands coordinating the metal ion. When only one of such derivatives is present, the coordination sphere is completed by 2,2'-bipyridines [44,70-72,75-80], Cl⁻ [70,77] or CO [70]. In the opposite situation, three bipyridine-(oligo)thiophene derivatives are inserted in order to complete the metal coordination sphere [44,67-69,73-75,77]. In this last case, the conductivity of the relevant metallopolymers was found to be significantly high [44] due to the formation of crosslinked polymers.

Zotti et al. [74] found that compounds containing metal complexes with three bipyridine ligands are not very stable in some cases. Compounds like 5 present different behaviour depending on the nature of the metal. In the case of both Fe(II) and Ru(II) the relevant polymers form, but the oxidative process induces loss of metal coordination with one bipyridine ligand; this effect is ascribed to bipyridine protonation by protons released in the chain propagation at the terminal EDOT rings. Interestingly, the film grows thanks to its redox conductivity, due to the closeness of the potential at which the organic chain propagates to the standard potential of the Fe(III)/Fe(II) and Ru(III)/Ru(II) redox couples. This is not the case for Co(II) and Ni(II), so that the first step of chain propagation forms an insulating layer on the electrode and the growth is stopped.

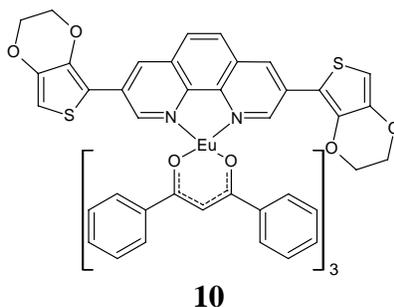
2,2'-Bipyridine ligand directly connected to oligothieryl derivatives was also employed for the formation of conducting *metallorotaxanes* [81,82], i.e. of cyclic molecules 'threaded' by cyclic fragments (see compound 7). After polymer electrogeneration, the macrocycles, containing either redox active metal centres, e.g. Cu(I), or redox inactive ions, e.g. Zn(II), are irreversibly linked by the polymer. The trapping cavity preserves its own structure also after removal of the metal ion template. With proper choice of the derivative, the complexation process is reversible and in some cases even independent of the nature of the original metal ion inserted [82].



Different authors [83-87] performed analogous investigations on bisphenanthroline-based metallorotaxane (see compounds 8 and 9 as representative examples). They initially focused their studies on derivatives similar to compound 8, characterised by a 1,10-

phenanthroline ligand, substituted in 2 and 9 positions by bithienyl residues [83-85], in order to gain a direct electronic coupling between the metal centre and the conjugated moiety. On the other hand, the final polymeric structure resulted quite flexible after removal of the metal ion: complexation is again possible only if Li^+ is present during de-complexation. Such an ion probably acts as an ionic scaffolding maintaining the topography of the coordination site. Any attempts to replace Cu(I) ions with different metal ions [84], such as Co(II), Zn(II) and Ni(II), or to directly synthesise metallorotaxane with these metal ions failed, probably due to the poor affinity to phenanthroline of these metals.

Substitution of 1,10-phenanthroline with bithienyl residues in 3 and 8 positions [86,87], as in the case of compound 9, leads to metallopolymers containing a linear conjugated backbone, which results in an enhanced conductivity with respect to the previously reported U-shaped derivatives. In this case, the removal of the metal centre results in a more rigid structure, which still allows complexation, also in absence of Li^+ ; the introduction of a metal ion different from the original one, such as Co(II), was also possible with these derivatives. More recently [88], the same authors reported the first results on penta-coordinated metalloroxanes containing one terpyridine residue replacing one phenanthroline moiety.



Only few 1,10-phenanthroline oligothiophene derivatives not belonging to the family of metallorotaxanes were investigated in view of possibly leading to metallopolymers [89-91]. By following one of the proposed approach, applied in the case of compound 10 [91], only one phenanthroline, inserted between two thienyl derivatives, is exploited in order to coordinate Eu(III) metal ions; in this case, the metal coordination sphere is completed by different diketonate groups, allowing the formation of a linear metallopolymer with interesting photoluminescent properties.

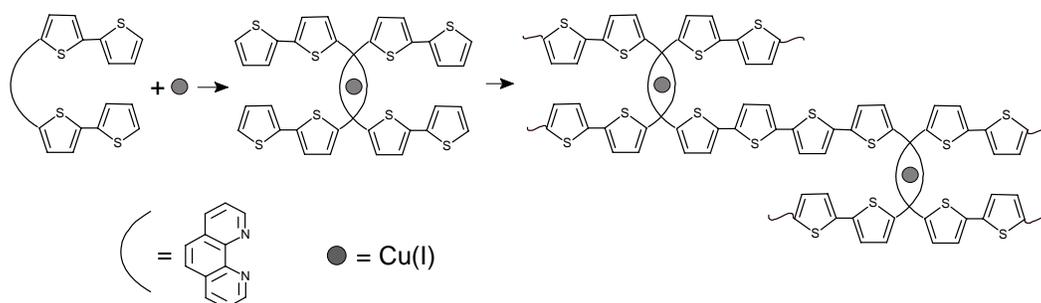
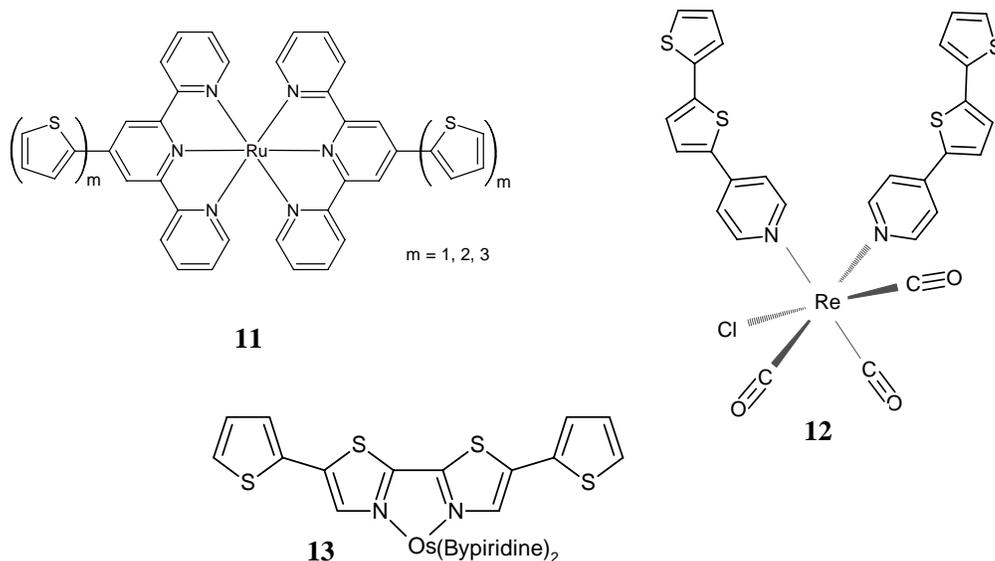


Figure 5. Schematic representation of the synthetic strategy to obtain 1,10-phenanthroline bithiophene-based metallopolymers

A different synthetic approach is reported in Figure 5; it is based on the use of two 2,9-bis(oligothienyl)-1,10-phenanthroline precursors that complete the Cu(I) coordination sphere [89,90]. Due to steric reasons and to the occurrence of oxidation at accessible anodic potentials, only bi- or ter-thiophene derivatives are suitable to lead to corresponding conjugated metallopolymers.

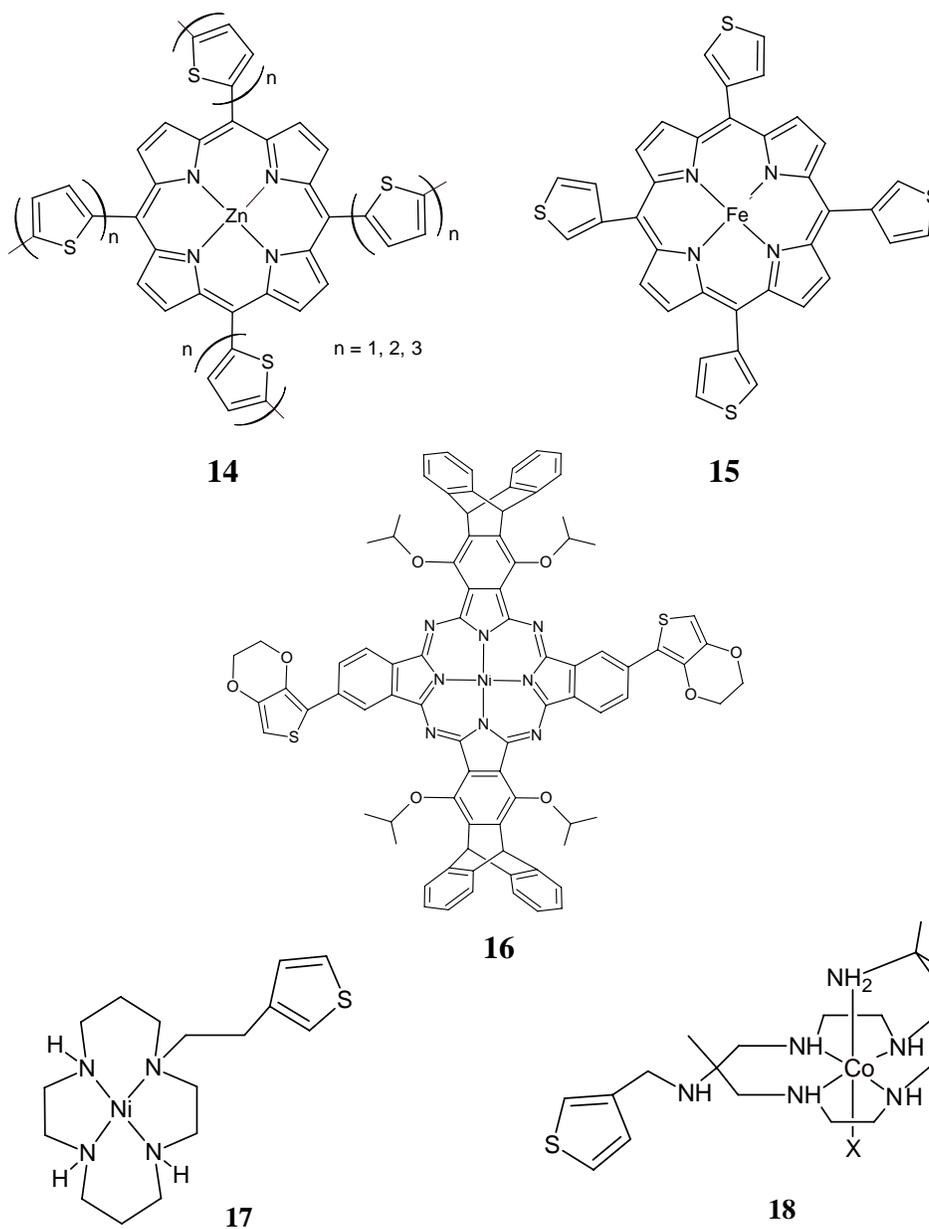


Similarly to the corresponding bipyridine derivatives, $[\text{Ru}(2,2':6',2''\text{-terpyridine})_2]^{2+}$ and $[\text{Os}(2,2':6',2''\text{-terpyridine})_2]^{2+}$ chromophores have also shown luminescence properties. Even though both luminescence efficiency and excited state lifetime are significantly poorer in comparison to the relevant 2,2'-bipyridine complexes [92], the substituents to the terpyridine ligand significantly improve the luminescence properties [92,93]. In particular, it was observed that the use of 2,5-(oligo)thiophenediyl linkers, bridging neighbouring $[\text{Ru}(\text{terpyridine})_3]^{2+}$ centres (compound 11), definitely improves the luminescence efficiency [92]. When these kinds of terpyridine-(oligo)thienyl derivatives are electrochemically oxidised [92-98], linear metallopolymer can be obtained. As expected, the results indicate [97] that the charge transport rates can be significantly enhanced by extending the length of the oligothiophene bridge from two to six Th rings.

As a last example of exploitation of the well known coordination ability of pyridine moieties with respect to different metal ions, new species have been recently synthesised, in which two single *pyridine* (bi)thiophene derivatives coordinate Re(I) or Pt(II) metal centres [99]. Compound 12 represents one of the proposed molecules. This derivative can be polymerised under oxidative conditions; similar behaviour was observed for the corresponding Pt(II) derivative.

2,2'-*bithiazole* also represents an attractive metal ligand for the formation of different metallopolymer [45,100-102], thanks to its chemical similarity to 2,2'-bithiophene and to its complexing ability, similar to bipyridine. In all the examples reported in the literature a bithiazole derivative bridges two Th rings involving α - α' junction. The resulting adduct has been reacted with metal ions in 1:1 stoichiometric ratio, obtaining metal complexes similar to compound 13. The following polymerisation process, although found to be quite difficult due

to the high potential values required [45,100,101], leads to linear metallopolymers. Unfortunately, p-doping of the polymer backbone only occurs at very high potentials, where irreversible overoxidation of the organic structure also takes place [101,102]. Moreover, no electronic coupling between neighbouring metal sites was found to be operative in these kinds of metallopolymers [101,102].



A different class of nitrogen-based ligands consists of *macrocycles*, such as porphyrin, phthalocyanine and cyclam. The interest to these systems derives from the outstanding stability of the complexes formed and from the delocalisation of the electrons within the macrocycle.

Moreover, polyazamacrocycles can host various transition metal cations in different redox states, being thus potential good redox mediators. *Porphyrin* complexes have been explored for the formation of different metallopolymers, due to the variety of reactions catalysed by metal porphyrin complexes, such as epoxidations, hydroxylations and other oxidation reactions [103]. Moreover, metal porphyrins are the active site of many different biological species containing a heme group, such as cytochrome and peroxidase. The immobilisation of (metallo)porphyrins in the frame of polymeric matrices is therefore an attractive way to create redox-active materials for catalysis and, when deposited on an electrode surface, for electrocatalysis and even for photoelectrochemistry. In particular, PTh derivatives directly connected to porphyrin moieties have been synthesised and studied for application in electrocatalysis [49] and for use in sensor devices [47,48,52].

With reference to Figure 4, also in the case of porphyrin-based metallopolymers a number of different approaches has been adopted. In a first one, the tetraphenyl porphyrin unit is covalently linked to the β -position of the polymer backbone *via* a long oxoalkyl chain (Type I) [47-49,104,105]. Quite interestingly, Bäuerle et al. [49] found that functionalisation of the PTh chain by complexed porphyrin can be also achieved on the pre-electrogenerated pure organic polymer film.

Alternatively, the porphyrin has been directly attached to the β -position of two Th rings (Type III) [50,52]. The polymerisation process leads to a material where the porphyrin acts as a cross-linker connecting two polymer chains. Similar structures were also achieved using α -substituted Ths (Type IV) [106,107], providing linear metallopolymer chains, where the porphyrin is inserted within the polymer chain. Finally, tetrasubstituted porphyrins were linked with four (oligo)thiophene residues by exploiting either the α (compound 14) [108,109] or the β (compound 15) [110] positions. In this case, the polymerisation process leads to a two dimensional polymer, with porphyrin moieties bridging oligo- or poly-thienyl chains. While oxidative polymerisation of meso-tetrakis(3-thienyl)porphyrin is claimed to be possible [110], resulting in a completely insoluble material, the polymerisation of the analogous 2-thienyl derivative did not produce homopolymers; the formation of the sought polymeric material was only possible when bi- or ter-thienyl derivatives were used [108,109,111]. The advantage of using 3-thienyl derivative was also demonstrated with respect to the conductivity of the resulting material, which is significantly increased in comparison to the relevant 2-thienyl derivative [110], thanks to the possibility of delocalisation of the π electrons along the PTh chain.

Despite the number of papers concerning Th-porphyrine metallopolymers, to our knowledge only one paper reports on the electrochemical generation of a metallopolymer containing *phthalocyanine* moieties coordinated with Ni(II) (compound 16) [112]. The scarce number of articles reporting on this kind of metallopolymers can be related to the fact that only *trans* bi-substituted phthalocyanine derivatives undergo polymerisation.

As a final tetraazamacrocyclic ligand used for the formation of metallopolymers, *cyclam*, i.e. 1,4,8,11-tetraazacyclotetradecane (compound 17) [113-115], should be mentioned. Among different metal ions, the authors selected Ni(II), since the relevant cyclam complex is very stable and reversibly redox-active in the potential range where PTh chain is in the conducting state. In all the examples reported in the literature, the macrocycle is connected to one of the Th β positions through an alkyl spacer, in order to avoid steric hindrance between neighbouring monomer units. While Sable et al. [113] found that polymer films on the

electrode can be obtained by electrooxidation of this kind of monomers, Higgins et al. [114] report that only soluble oligomers can be obtained by oxidation. In order to obtain a polymeric deposit from these derivatives, a co-polymerisation with 3MT was necessary [114]; the composition of the resulting co-polymer was roughly estimated by integration of the current under PTh and Ni(II)/Ni(III) redox signals. Analogous procedure was adopted for a similar $[\text{Ni}(\text{cyclam})]^{2+}$ complex, covalently bounded to the saturated ring of EDOT [115]. The addition of chloride ions to the electrolyte solution used for the electrochemical characterisation causes the appearance of a new oxidation response ascribable to the formation of a pseudo-octahedral $[\text{NiCl}_2(\text{cyclam})]$ structure.

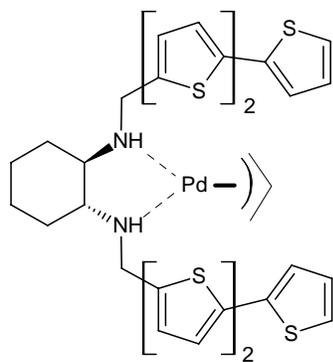
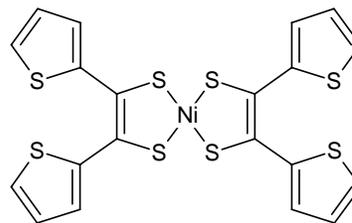
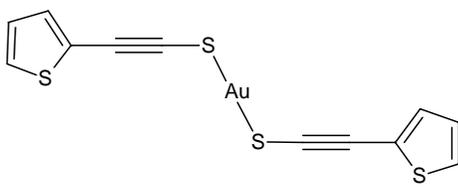
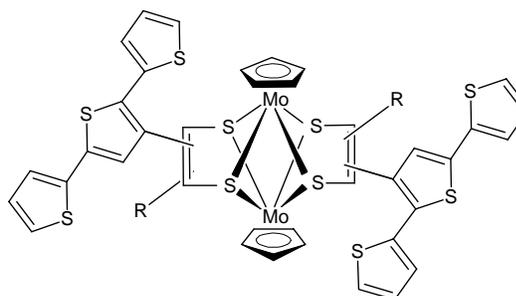
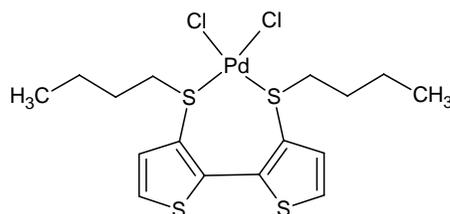
Similar to cyclam, 1,4,8,11-tetraazacyclotetradecane-6-amine was also studied as Th substituent for the coordination of Co(III) ions [116], as reported for compound 18. Also in this case, the polymerisation of the monomer did not result in electrodeposition onto the electrode surface. The composition of the co-polymer obtained in the presence of EDOT was determined through XPS analysis, on the basis of the Co(III) to S ratio.

The versatility of nitrogen in coordinating different metal ions was also exploited in compound 19 [117] synthesised in order to obtain an heterogeneous organometallic catalyst for Suzuki cross-coupling [118]. The possibility to stably anchor a polymer film on an electrode surface through a simple electrochemical oxidation allows facile removal of the catalyst from the solution of synthesis.

Although attracting much less effort than nitrogen-based ligands, different sulphur-based ligands, under the form of dithiols and dithioethers, have also been used for the formation of metallopolymers. As to *dithiol* complexes, they deserve attention [119-122] thanks to their aromatic character, which allows electron connection between the polymer π -system and the metal centre; moreover, the resulting metallopolymers can be reduced, i.e. n-doped, at relatively low potentials. Dithiol substituted Ths reported in the literature were investigated when complexing Ni(II) [119-121], Pd(II) [120,122] and Au(III) [120,122]. After the pioneering work of Pickup [119], who reported the formation of a polymer starting from compound 20, different approaches have been followed in order to improve the properties and, in particular, the conductivity of the relevant metallopolymers. However, the use of both the 3-thienyl derivative [121] and terthiophene, instead of a single Th ring [120], leads to poorly conductive films. The X-ray structure of one of these building blocks [121] revealed twisting of the Th units out of the plane of the dithiolene moiety, which is a possible explanation to the poor conductivity observed. Moreover, the presence of Ni(II) metal ions affects the oxidation processes in charge of the PTh chains [122]: the presence of these metal centres induces charge localisation at the oxidised metal centres, lowering the electron density of the PTh ligand and significantly shifting the anodic processes to higher potentials.

A 2-alkynethiol substituted Th was used for synthesising a metallopolymer containing Au(II) ions (compound 21) [123]. The resulting polymeric film shows a surprisingly low oxidation potential, when considering the shortness of the bithienyl spacer between two adjacent Au centres; this fact can be accounted for by a significant degree of conjugation throughout the entire chain, even involving the Au centres.

Finally, dithiol substituted terthiophenes were used for anchoring a Mo cluster (compound 22) [124]. The resulting metallopolymer shows interesting electrochromic property, well distinct from that of the pure organic residue, ascribed to significant electronic interaction between Mo sulphide cluster units and polymer π -backbone.

**19****20****21****22****23**

Metal coordination with *thioethers* derivatives similar to compound 23 were also investigated, due to their ability to complex soft transition metal ions [125] such as Pd (II) [51,126-128] and Pt (II) [126]. These works take advantage of the properties of alkylsulphanyl-substituted PThs, which show a particularly reduced band-gap with respect to most part of the studied PThs, and are stable both in p- and in n-doped states [129-132]. Thanks to the presence of two sulphur atoms on β -carbons of the same Th unit [126,128] or on adjacent Th rings in head-to-head bithiophene unit [51], the alkylsulphanyl substituted PThs easily coordinate metal centres, even when deposited on an electrode surface. The metal-ligand interaction was found to deeply modify the electronic structure of the material, with respect to the pure organic polymer [51], and even to quench the fluorescence emission typical of these polymers almost completely, when one Pd (II) ion per structural unit is added to the solution. Unfortunately, any attempts to synthesise the fully coordinated metallopolymer starting from the relevant Th and bithiophene derivatives failed, due to partial charge transfer to the Pd centre [51,126,128]. On the other hand, the deep investigation of

these building blocks was of basic importance in order to clarify the chemical and electronic structure of the metallopolymers [51,126,128].

As a very different metal ligand, Mirkin and Wolf separately worked on electropolymerisation of diphenylphosphine derivatives of terthiophene, differently coordinated with Pd(II) [133,134], Rh(I) [135] and Ru(II) [136,137] centres, such as those schematised in Figure 6. The interest to these derivatives is ascribed to their possible capability to act as hemilabile ligands with respect to the coordinated metal [138]. In particular, they can be reversibly switched from bidentate (type *b* in Figure 6) to monodentate (type *a* in Figure 6) coordination modes, by reacting with strong σ -donor ligands, such as CO. This aspect is at the basis of possible applications of these materials in the field of sensors. The different derivatives contain a phosphine moiety directly linked to the Th ring, allowing strong electronic coupling between the metal and the conjugated backbone; the reaction with the σ -donor ligand, e.g. a potential analyte, results in significant changes of UV-Vis [134,139] or FT-IR [133,137] spectra and of metal-centred electrochemical system [139]. Particularly promising are oligothieryl derivatives similar to type *b* in Figure 6, where the Ru(II) coordination set is completed by two 2,2-bipyridine moieties; these complexes can be forth and back switched from a P,S (type *b*) to a P,C (type *c*) coordination modes, in the presence of a basic or acid reactant, respectively [139].

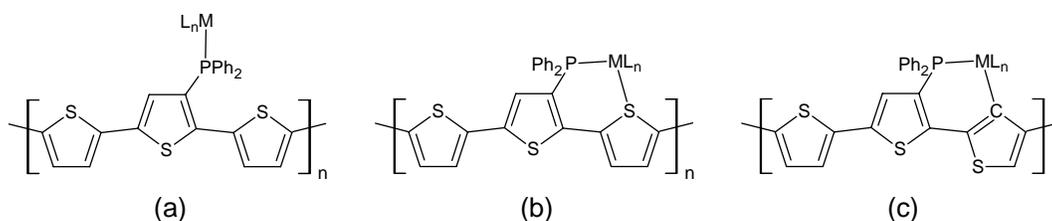
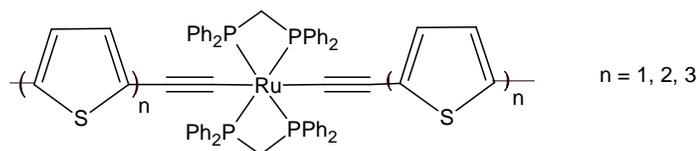


Figure 6. Some possible coordination modes for phosphino-terthiophene derivatives with respect to different metal ions: (a) monodentate phosphine, (b) bidentate (P,S) and (c) bidentate (P,C). [adapted from ref. 184]

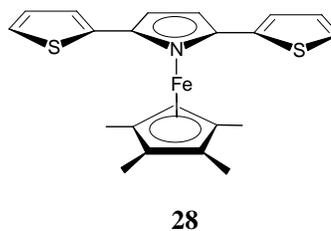
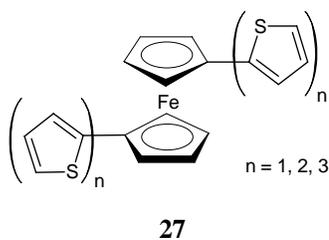
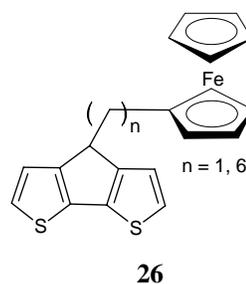
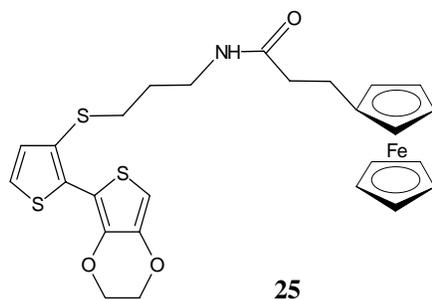
Diphenylphosphine was also a ligand for Ru(II) metal centres in bis(oligothienylacetylide) complexes **24** [140]. Only when bi- and terthiophene derivatives were used as the alkyl residues, a polymer film can be obtained on an electrode by electrochemical oxidation of a monomer solution. Electrochemical and UV-Vis analyses indicate that the π -system of the oligothieryl moiety electronically interacts with Ru centres.

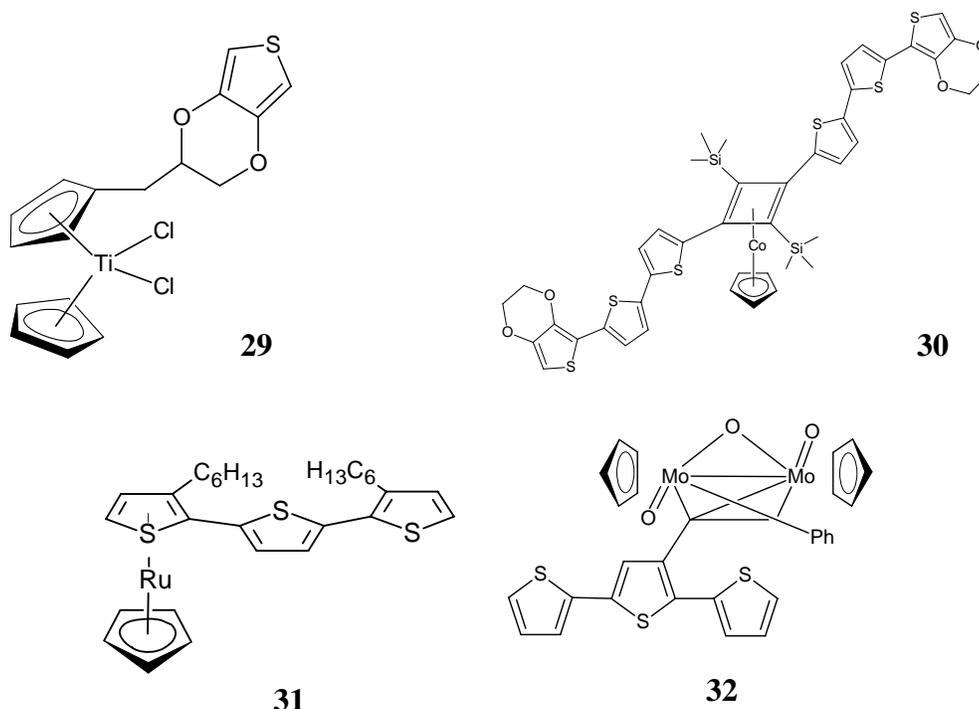


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Among different electroactive metal complexes, ferrocene group has been deeply characterised and stably anchored to electrode surfaces [42] for possible applications as redox

mediator in electrocatalysis. Several attempts have been carried out in order to covalently link ferrocene groups to Th, either electronically separated by a long alkyl chain [141,142] or electronically connected through an ethylene spacer [143,144]. In all cases, including the case of EDOT derivative [142], electropolymerisation leads to poorly conductive films. To overcome this drawback, materials with interesting properties have been obtained by copolymerisation of similar Th derivatives with 3MT [141], pyrrole [143], 3-butylthiophene [144] and hydroxymethyl-EDOT [142]. On the other hand, homopolymers were obtained from similar ferrocene structural units when starting from the relevant bi- [145] and terthiophene [143] derivatives. Compound 25 is a different ferrocene-derivatised bithiophene precursor, which combines an EDOT moiety with a Th ring bearing the functional group in the internal β -position, *via* a sulphide linkage [146]. As an alternative, different condensed bithiophene derivatives similar to compound 26 have been synthesised, in order to lower the potential value required for the formation of the relevant homopolymers [147-150]. All these bithienyl precursors can be more easily electropolymerised, resulting in stable electroactive materials which retain the well-defined voltammetric signal typical of the ferrocene/ferricinium ion redox couple. As an alternative, ferrocene units were also directly inserted into a PTh chain by exploiting Th α positions [151-153], as reported for compound 27. With this respect, since the oxidation of the compound containing one single Th outer moiety did not lead to the formation of the desired metallopolymers, monomers bearing bi- and terthiophene groups were successfully synthesised. Similar 1,1'-dithienyl substituted ferrocene structures lead to polymers with segmented structures, where the oxidation potential of the oligothieryl moiety is significantly higher with respect to the ferrocene/ferricinium redox couple. Alternatively, aza-ferrocene derivatives similar to compound 28 were synthesised [154]; they are realised by substituting a pyrrole for one cyclopentadienyl ring. The polymerisation of similar derivatives, involving the outer Th rings, results in the formation of linear metallopolymers, characterised by a complete electronic delocalisation along the polymeric chain, also involving the metal centres.





Similarly to ferrocene, *titanocene* was also linked to a PTh chain by electrochemical oxidation of compound 29 [155]. Despite EDOT was chosen for this purpose, since the reduction peak of the relevant polymer, i.e. PEDOT n-doping, is very close to the reduction of titanocene, the charge transfer between metal centres inside the metallopolymer film was found to occur through electron hopping mechanism. The difficulty observed in the charge transfer was ascribed to steric hindrance of the Ti complex substituent, coupled with rigidity of the connecting arm; on the other hand, also the formation of short polymer chains or of polymer chains characterised by quite short conjugation/chain length is claimed to be the possible origin of the poor conductivity of the material.

Cyclobutadiene cobalt cyclopentadiene complexes directly connected to the α positions of oligothiophenyl units were also synthesised [156]. Despite the wide number of derivatives differently substituted at the remaining positions of the cyclobutadiene moiety, only compound 30 can afford a polymer film still containing intact Co complex, as evidenced through electrochemical investigations. This fact is ascribed to the presence of two EDOT outer units that allow the oxidative polymerisation to occur at potential values below that of the Co(I)/Co(II) standard potential.

Several oligothiophene derivatives were also connected to a Ru(II) cyclopentadienyl moiety by exploiting the coordinating ability of Th ring (η^5) acting as the second sandwiching ligand, as reported for compound 31 [157]. Although PTh films can be obtained through electrochemical oxidation of these oligothiophene derivatives, none of the relevant Ru(II) complexes leads to the metallopolymers sought.

Organometallic complexes based on Mo₂ or Co₃ clusters were also linked to terthiophene moieties [158-160], as in the case of compound 32. Despite the high potential required by the oxidation of the oligothiophenyl moiety, probably due to electron withdrawing by the cluster, the electrochemical oxidation afforded an electroactive polymer film on the electrode surface in

any cases. The materials are characterised by strong electronic interaction between the organic and the inorganic moieties.

3. INCLUSION OF METAL IONS INSIDE THE POLYTHIOPHENE MATRIX

At variance with the previously reported class of materials, transition metal complexes were also included as such into the PTh matrix, i.e. in absence of any covalent bonds linking the ligand to the polymer chain. Taking advantage of the cationic nature of the p-doped polymer chains constituting the polymer deposit growing on the electrode, the host polymer material can embed anions containing transition metals either during electrogeneration or in subsequent doping/de-doping electrochemical cycles performed in a solution where the relevant monomer is absent and the anionic metal complex is present.

In the former case, the PTh derivative is electrogenerated in the presence of a complex anion of the transition metal, which acts as the counterion of the arising positively charged polymer chains. If these anions possess big enough size, they are retained inside the polymer deposit when the electrode system works in polymer charge and discharge cycles [161]. In this case, the charge compensation required by the redox processes undergone by the polymer mainly involves the cations of the supporting electrolyte, that are included and expelled during the discharging and the charging processes, respectively. A possible drawback to such an approach arises from the necessity to electrogenerate the polymer in organic media, typically in CH_3CN , due to the low solubility of the relevant monomer in water, while many common transition metal anions are only soluble in aqueous systems. Actually, as regards the inclusion of complexes in parallel to electrogeneration, literature reports only concern the inclusion of $[\text{Fe}(\text{CN})_6]^{3-}$ (FeCN) anions into a PEDOT organic matrix [162-169], whose EDOT relevant monomer is soluble in aqueous media. The inclusion of this anionic species can be very simply detected through voltammetric tests, thanks to the well known reversible response it gives rise. Even if it was observed [163,167] that FeCN anions are not stably entrapped into the organic matrix, due to anion exchange process with Cl^- anion in the solution, these materials revealed to be interesting for application in the field of both potentiometric [162,169] and amperometric sensors [162,164]. In conclusion, this method leads to fast and easy formation of hybrid materials, but it is conditioned by the limited number of big enough anions that contain metals of interest. As an alternative method proposed, 'bare' transition metal ions were also embedded inside the polymer [170] by performing the polymerisation on a substrate made of the metal of interest, such as Mo, Ni and Fe. The application of the positive potential required for polymer electrogeneration implies 'dissolution' of the metal substrate: the relevant cations are thus trapped inside the polymer matrix.

Negatively charged ions can be also inserted into the polymer matrix by ion-exchange with counterions that were entrapped inside the film during previous polymer electrogeneration. In this case, also PTh derivatives electrogenerated in organic media, such as P3MT, can be suitable for formation of hybrids. First examples of hybrid materials generated according to such a procedure concern the inclusion of $\text{Au}(\text{CN})_2^-$, $\text{Pt}(\text{CN})_4^{2-}$, IrCl_6^- and PtCl_6^- into P3MT electrode coatings [171,172]; the aim was to improve the conductivity

of the host organic matrix. However, more interesting materials were obtained by inserting FeCN anions, for the formation of PTh/Prussian Blue (PB) composites [173,174]. In this approach, a PTh derivative is electrogenerated in a first step in a CH₃CN solution; in a second step, PB is electrogenerated under potentiostatic conditions in a solution containing both FeCN and FeCl₃. FeCN anions electrostatically interact with polarons on the electrode surface and Fe(III) ions are reduced to Fe(II); these processes lead to formation of PB, which is uniformly distributed inside the porous structure of the polymer film.

Due to well documented electrocatalytic properties of PB [175], its stable inclusion inside a polymer host material has been the subject of many investigations. By reversing the order of the two deposition steps just described, a PB/PTh bilayer film can be obtained [176,177]; to such a scope, the conventional deposition of PB onto the electrode is followed by the deposition of a second layer, consisting of a PTh derivative. In this case, the entrapment of the inorganic material, under and also inside the host organic matrix, confers stability to PB both in neutral and in alkaline solutions, increasing the number and effectiveness of possible applications. PEDOT/PB electrode coatings were also obtained starting from PEDOT/FeCN films [165,166,168,169,178]. In a first approach [166], this electrode coating, immersed in a solution containing KCl, was submitted to a multicyclic polarisation in the anodic region. It was observed that the electrode coating undergoes an electrochemical reordering: the anodic peak system typical of FeCN progressively lowers till being no more detectable, and a new peak system, typical of PB, appears. The electrochemical behaviour indicates the formation of PB units inside the polymer film. In a different synthetic approach, PEDOT/PB modified electrodes were obtained by an analogous PEDOT/FeCN reordering process, performed however in a solution containing FeCl₃ [168,169,178]. In the de-doping process the polymer loses positive charges and charge compensation implies both partial exit of FeCN and partial parallel inclusion of Fe(III) or Fe(II) from the solution. A similar procedure was also carried out in CoCl₂ [168,178], NiCl₂ [168,178] and CuCl₂ [165] solutions, leading to the formation of the relevant metal hexacyanoferrate. Interestingly, at variance with PEDOT/FeCN, electrode coatings containing metal hexacyanoferrate exhibit good stability under repetitive doping-dedoping processes in aqueous KCl solutions.

By considering the insertion of cations into PEDOT polymer host matrix, occurring during the polymer de-doping process, the procedure just described was also followed for the insertion of ferricinium ion [179] and [Ru(NH₃)₆]³⁺ [167]. However, while ferricinium ion is stably entrapped inside the polymer film, hence affecting the properties of the whole material, Ru(III) complex cations are released in the first subsequent oxidation step. Not surprisingly, the dimension and charge of the complex anions, as well as the conditions under which the polymer is grown, are very critical with this respect.

Different hybrid materials containing transition metal ions were also obtained through non-electrochemical approaches. For example, bilayer films were obtained depositing Cu- or Co-phthalocyanine, either as such or included in a sol-gel matrix, onto an electrogenerated P3MT film [180,181] by an *ad-hoc* modified dip-coating procedure; by exploiting the metal phthalocyanines electrocatalytic properties, these modified electrodes show interesting behaviour with respect to H₂O₂ electroreduction.

Very interesting hybrid materials were also obtained through a chemical approach. In the first case reported in the literature [182] chemically prepared poly(3-methyl-4-octylthiophene) was blended with phosphorescent Ir(II) or Pt(II) complexes. The resulting materials act as the active layer of a light-emitting diode. The photoluminescence and

electroluminescence of the material resulted dependent on the complex concentration. In the second case reported [183], the insertion of Fe(III) species inside a chemically prepared poly(3-octylthiophene) was obtained through oxidation, by H_2O_2 , of the organic material in the presence of anionic iron oxalate. The presence of the inorganic component inside the polymer matrix significantly increases the conductivity of the resulting material with respect to the pure organic one, as estimated by impedance spectroscopy measurements.

4. ZERO-VALENCE METAL INSIDE THE POLYTHIOPHENE MATRIX

The insertion of zero valence metals into a PTh matrix has been extensively investigated. Metals are embedded under the form of clusters, nanoparticles, or larger aggregates. An unambiguous distinction among these three forms is not straightforward at all, since many authors proposed slightly different classifications [185].

The term *cluster* is commonly used to indicate aggregates of few atoms, usually below 20 atoms, whose size is usually below 1 nm. In clusters, metal atoms are normally connected through metal-metal bonds, although non-metal atoms, such as O, forming bridging bonds between metals, are sometimes present. In other words, a cluster can be defined as an aggregation of (few) metal atoms strongly interacting electronically with each other.

Nanoparticles (NPs) can be defined as the constituents of extremely fine powder, generally considered transitional between the *cluster* and *bulk* scales. Although only the NPs possessing a size below 20 nm exhibit a surface/volume ratio much higher than that of the bulk material, the term ‘nanoparticles’ is sometimes used in the literature even for particles with a size up to 1 μm . Proper NPs possess a polyhedral shape, so that a high fraction of atoms is localised in the correspondence to defects such as vertexes and corners. This aspect accounts for their particular properties with respect to the relevant bulk material; at increasing the dimension, the NPs tend to a spherical shape, losing the mayor part of their peculiarities. Other kinds of nanostructures possessing at least one dimension below 1 μm have been reported by the literature, such as *nanowires* and *nanoshells*. However, the number of studies dealing with the formation of composite materials of similar nanostructures with PTh is so limited that they are discussed here together with the NPs.

The term *large aggregates* comprises all the metallic structures possessing a size larger than 1 μm . In most cases, the shape of the aggregates is irregular, consisting of NPs in close contact with each other. Hence, the properties of aggregates are, to some extent, similar to those of the NPs.

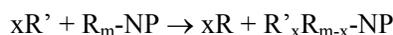
Metal Nanoparticles

Metals that are under the form of NPs possess very peculiar properties: in particular, the small amount of atoms confers the system (electro)catalytic properties by far superior with respect to bulk systems. In addition, confinement of the electrons in regions of nanometric dimension leads to special optical properties: as an example, Au NPs possess a colour ranging from red to violet, depending on the size and distance between adjacent NPs. Furthermore, a nanometric size leads to a significant reduction of the melting point. The procedures for the

synthesis of NPs have been extensively reviewed [186,187] and they will not be discussed here.

NPs, in particular made of Au, Pt, Pd and Cu, have been often used for the preparation of PTh-NP composites. In most cases, NPs actually consist of a metal core coated by a stabilising encapsulating layer, which is commonly constituted by organic species. In many cases, the resulting encapsulating cloud is formed by a monolayer of molecules adsorbed on the surface of the NPs, the strength of adsorption varying over a wide range. The encapsulating agent plays a number of roles, the most meaningful one consisting in the control of the growth of the NPs, i.e. of the mechanism of formation, mean size and size distribution, as well as solubility. The presence of the encapsulating layer is usually absolutely necessary to prevent aggregation of the NPs in solution, while such a stabilisation is not necessary when the NPs are generated directly on a supporting material.

The encapsulating agent can also be involved in chemical reactions [189-193]. In particular, the molecules of the encapsulating agents adsorbed on the NP surface (R_m -NP) can be (partially) replaced by molecules dissolved in solution (R'), e.g. by thiols, when characterised by stronger affinity to the metal [194,195]. The reaction, often called *place exchange* reaction, is as follows:



The substitution yield depends on a number of factors, such as *i*) relative strength of the adsorption of R and R' ; *ii*) steric effects, so that bulky R' residues are disfavoured in the displacement reaction.

The nature of the encapsulating agent and the possibility to undergo displacement are particularly important in determining the interaction of the NP metal core with the environment. The presence of a compact and strongly anchored encapsulating layer leads to NPs that poorly interact with the environment, since the diffusion of the species to the metal core is hindered. On the contrary, if the encapsulating agent is loosely bound to the NP metal core, it can be easily displaced by solvent molecules or by species dissolved in solution or dispersed in gas phase. The displacement is also important with respect to the (electro)catalytic properties of the PTh-NP composites, since activation of catalysis requires easy access to the NP metal core.

Interaction of Thiophene Derivatives with Metal Surfaces

The interaction of Th derivatives with metal surfaces is particularly important in the context of PTh-NP composites. The PTh matrix can interact with the outer region of the NPs, i.e. with the encapsulating layer, so that the nature of the interaction is strongly dependent on their characteristics, as discussed below. Alternatively, PTh species can interact directly with the NP metal core through adsorption of PTh chains on the metal core surface. A strong interaction between PTh and the NP surface atoms is often obtained through a place exchange reaction between a labile encapsulating agent and PTh chains. The arising of a strong interaction between the polymer matrix and the NPs prevents any leakage of NPs and increases the electrical conductivity of the composite material with respect to the pure organic

one. However, a possible detrimental effect of the presence of PTh matrix, as well as of the encapsulating agent, consists in hindering the access of species dissolved in the solution to the NP metal core.

An exhaustive understanding of the actual interaction between PTh chains and metal NPs is not straightforward at all. On the contrary, the adsorption geometries of Th derivatives have been relatively deeply investigated on planar surface of metals, especially in the case of noble metals. By considering that the adsorption geometry is supposedly similar in the two cases, the models obtained for (oligo)thiophene adsorption on planar surfaces are generally considered in order to understand the NP-PTh interaction. Some reports, in particular regarding the adsorption of thiol molecules on Au NPs, confirm that this assumption is valid [196,197], although some minor discrepancies due the polyhedral shape of the NPs and the presence of defects on NP surface have been evidenced.

Adsorption processes of Th derivatives can originate either fairly ordered monolayers, i.e. Self Assembled Monolayers (SAM) or deposits disordered at molecular scale. The latter situation generally occurs when long oligomers or even polymers are used. A SAM consists of a monolayer of molecules adsorbed on a substrate surface [198,200]. A self-organisation process can take place so that, after the adsorption on the substrate, the final structure of the SAM consists of a well-ordered thin film. In principle, this holds both with respect to facets of bulk substrates and of NPs. A typical species suitable for the formation of SAM (Figure 7) possesses a *head group*, which is physis- or chemisorbed on the substrate, and a *tail group* at the opposite side of the molecule, which is at the interface between the thin film and the external environment (vacuum, air, or a liquid phase). A *spacer* connects these two groups. The packing density is normally high, so that the interactions between adjacent spacers play a basic role in conditioning the final structure of the SAM. It is possible to tune the chemical and physical properties of similar thin films by changing the chemical composition of the head and tail groups and of the spacer.

As to the polymers, the adsorption process leads to the anchoring of short segments of the polymeric chain, called trains, to the substrate; the rest of the backbone forms loops and tails (Figure 8). This behaviour, which is common to the vast majority of the polymers, has been reviewed, e.g., in ref. 201.

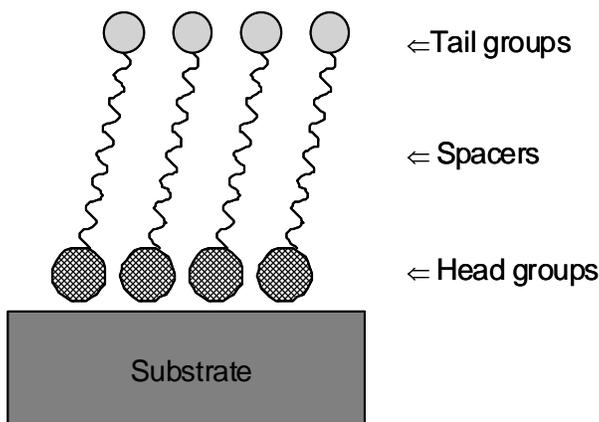


Figure 7. The basic structure of a SAM.

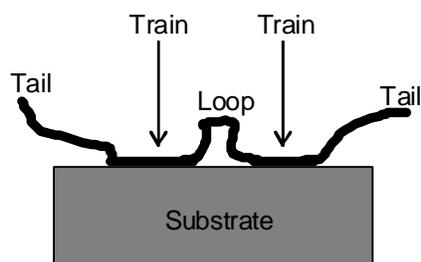


Figure 8. Typical adsorption geometry of a polymeric chain.

Th rings are considered essentially chemically unaffected by the adsorption process on metal surfaces. However, some authors reported that Th derivatives can react during the process, forming species such as atomic S and thiols [202-205]. Unfortunately, these studies are generally limited to planar metal surfaces, normally based on Pt, Au, Ni and Mo, and to very simple Th derivatives. Hence, the nature of the interface of both the bulk metal and the NP metal core surfaces with Th derivatives is far from being exhaustively investigated.

Effect on Conductivity of Nanoparticle Aggregation or Coalescence

It is well known that a finely divided powder spontaneously tends to reduce its surface to volume ratio, leading to an increase of the dimensions of the (nano)particles. In the case of NPs, two processes can be operative, i.e. aggregation and coalescence [186,206]. Aggregation consists in the formation of ensembles of NPs due to the interaction among the NP cores or among the encapsulating layers of adjacent NPs. By aggregation, the NP cores normally preserve their own individuality. On the other hand, coalescence consists in the formation of NPs possessing cores larger than those of the starting NPs, so much so that they can even lose the characteristics of proper NPs. If the coalescence process involving a group of NPs is complete, the final shape of the resulting system may even be no more polyhedral, becoming almost spherical for a high enough number of coalescing NPs. Coalescence can be only partial, since completing the process normally requires a thermal treatment. Partial coalescence usually leads to the formation of a large number of different structures. Actually, a precise distinction between aggregated or partial coalesced NPs is rather difficult and often speculative, especially when NPs are part of a composite.

In the case of metal NPs relatively close to one another in the composite materials, the metal cores can form charge percolation pathways inside the composite, as often observed in the case of insulating polymers containing conducting particles, such as carbon black, as fillers [207]. Alternatively, NPs that are relatively far from one another can be electrically in contact, thanks to the presence of conjugated organic molecules electrically bridging the metal cores. It is worth noticing that insulating encapsulating agents, often employed for the chemical synthesis of the NPs, can severely hinder the interaction between the polymer chains and the metal cores and, therefore, affect the electrical conductivity of the composite as a whole [208]. With this respect, the use of small molecules loosely anchored at the NP surface constitutes a good choice, since they are substituted by polymeric chains through a place exchange reaction. Alternatively, some authors suggest the use of encapsulating molecules

consisting of a head group stably anchored at the metal core surface and of an oligothiophene as a conducting tail that can be involved in the polymerisation leading to the organic component, forming a 'wire' between two metal cores [208-210].

4.1. Methods for the Preparation of Composites Containing Clusters, Nanoparticles and Large Aggregates

A variety of methods has been proposed for the preparation of PTh-NP composites. A tentative classification is reported hereafter. All the composites described in this section have been directly formed on a substrate or deposited after the synthesis; however, it is worth noticing that literature reports a large number of additional soluble composites that, in principle, could be easily deposited (see, e.g., ref. 211).

4.1.1. Electrodeposition of clusters, nanoparticles and large aggregates after polymer formation

Composite materials in which a polymer matrix embeds zero-valence metals can be very simply obtained by a two-step procedure consisting of metal electrodeposition onto/into a pre-formed polymer film. In a first step, the PTh derivative is electrogenerated on the electrode surface or, alternatively, a chemically synthesised polymer is dip- or spin-coated onto the substrate. In a second step, the electrode is immersed into a solution containing the metal salt and polarised at a suitably negative potential, in order to induce metal reduction, with consequent deposition onto the polymer outermost surface and into the pores of the coating. Despite the wide number of studies on composite materials synthesised by this approach, a deep understanding of the nature and size of the resulting inorganic structure is far from being exhaustive. For this reason, it is difficult to make a clear distinction among the formation of clusters, of (nano)particles or of nanoparticle aggregates; the general term *metal inclusion* is more properly used in this case.

Even if it is difficult to obtain a complete picture of the influence of the different synthetic parameters on the number, size and distribution of the metal inclusions obtained, it is possible to conclude that they are strongly dependent on the polymer film porosity and thickness, and on the actual oxidation state of the organic component. With this respect, it should be considered that metal reduction quite often occurs simultaneously to de-doping of the host polymeric material, which makes it poorly conducting. For this reason, a proper choice of the PTh derivative and of the electrochemical parameters for the metal deposition strongly influences the metal inclusion process and the relevant result [212]. Even if a detailed experimental study of these aspects was only performed for the case of polyaniline films [213], it is well reasonable to think, at least limitedly to the chemical common background of the two materials, to similar behaviour for PTh films. Metal inclusion leads to quite different metal deposits, depending on the neutral or p-doped state of the polymer film. In particular, when the polymer coating is basically insulating, the only way for the metal ions to be reduced is to diffuse into the porous structure of the polymer layer up to reaching the underlying conductive substrate and hence to form metal nuclei at the substrate/polymer interface. By prolonging the deposition process, the particle growth proceeds inside the

polymer pores. On the contrary, when the metal reduction occurs at a p-doped polymer surface, the nucleation step mainly occurs at the polymer/solution interface. It comes out that the polymer thickness and the more or less porous structure of the film, which depend also on the experimental parameters chosen for the polymer synthesis, play a role in the composition and structure of the resulting metal deposit. A porous morphology seems more suitable to the uptake of metal units not only on the polymer surface, i.e. in direct contact with the solution, but also inside the film, with consequent increase of the electroactive area.

The effect of the metal ion concentration on the feature of metal inclusions was studied in the case of P3MT [214]. In particular, it was observed that a fairly high Cu^{2+} concentration (1-3 M) results in Cu inclusions with few nm mean diameter, homogeneously distributed inside the polymer pores, while a lower concentration (0.01 M) leads to significantly smaller particles, mainly deposited near the metal substrate.

A high number of reports concerning the synthesis of composite materials by such an approach involved the use of P3MT [214-230], even if the deposition on PTh [231-237] and, more recently, on PEDOT [212,238-245] films was also attempted. All these polymer materials show high conductivity and suitable porosity to host metal inclusions at the same time. When polarised at a fixed suitable negative potential, the residual conductivity of the polymer material is often high enough to allow complete reduction of different metal cations, obtaining deposition of Pt [215,228], also as a preliminary step for a following deposition of a further layer consisting of Pb [228]. The deposition of Pt-Sn [223], Pd [212,235], Pt-Pd [230], Cu [216-218,220-222,225,242,243], Ni [220], Au [236,237] and Ag [215,236] was also performed.

In several cases, especially when long deposition times or highly negative potentials are required, the residual conductivity of the polymer is too low to permit effective charge transfer between the electrode substrate and the metal cations. This drawback has been overcome by adopting a procedure based either on potential pulses, i.e. alternating anodic and cathodic potentials, or on voltammetric cycles; upper and lower potentials are suitably chosen in order to induce p-doping and metal deposition on the still partially charged polymer, respectively. Metal electroreduction, in fact, is favoured by the residual conductivity of the polymer due to slow de-doping. By such a strategy, Pt [231-234,244,246] depositions were performed, also as a preliminary step for a second layer Pb deposition [232,233]. Pd [219,226], Cu [224,226], Ni [227] and Pt-Ru [245] were also deposited. The particle size is, in this case, also conditioned by the pulse duration, due to the competition between nucleation and growth processes. In particular, it was observed [219,224,226] that increasing the electrolysis time results in the formation of few large particles, while the application of short pulses results in the formation of many small clusters homogeneously distributed on the polymer surface. At variance with composite materials obtained by adopting a potential pulse procedure, the application of a fixed cathodic potential results in a very heterogeneous distribution of the metal inclusions, mainly confined on the external surface of the coatings [219].

The electrode polarisation in the presence of the suitable metal salt not always leads to reduction to atomic state [217,218,220,221,224-226]. For example, in the case of Fe(III) deposition on P3MT [221,222], the potential necessary to achieve reduction to metal state is too negative to be compatible with residual high enough doping level. The reduction of Fe(III) to Fe(II) only takes place, which lowers the inter-chain conductivity of the material ascribed to S-S bridges, which are effective through Fe(III), though not through Fe(II) ions.

On the contrary, an increment of the conductivity measured *ex-situ*, i.e. on the dried material, was observed by electrochemical reduction of CuCl_2 on P3MT films [217,220,222]. Also in this case, metal/polymer complexes, due to interactions between the partially reduced Cu(I) ions and S atoms of two adjacent polymer chains, are responsible for such an effect [214,218,220-222]. By carrying out metal reduction under different electrochemical conditions [224,225], the polymer material results modified by a dispersion of Cu(I) species, i.e. both Cu_2O and CuCl , as evidenced by XPS measurements. In any cases, by prolonging the cathodic polarisation of the electrode in CuCl_2 solution, the complete reduction to metal state with the formation of very small Cu clusters is evidenced [216-218,222]. The two-step reduction of Cu(II) ion is ascribed to the presence of Cl^- complexing anions, which induce a splitting of the redox process; accordingly, a single reduction process to metal Cu occurs when non-complexing SO_4^{2-} or NO_3^- anions are used [224,225].

Cu electrochemical deposition, carried out either potentiostatically or galvanostatically, was also studied on PEDOT hosting material [240,241]; the electrochemical reduction results both in deposition of Cu crystals, which are re-oxidised and removed from the coating in the following anodic electrode polarisation, and in the formation of a stable Cu/PEDOT adduct, due to interaction of Cu(I) with S atoms of the polymer chains. In particular, complete Cu reduction occurs for highly negative potentials applied, while Cu(I) stabilisation is favoured for less cathodic potentials. By application of suitably negative potentials to the modified electrode dipped in a solution not containing Cu(II) salt, stabilised Cu(I) centres inside the polymer film undergo further reduction to Cu(0) [241,242,244]. Cu(I) centres act both as nucleation points and as inclusions affecting the polymer electronic structure and consequent conductivity: their presence affects the electro-crystallisation process [242,243,247], favouring nucleation with respect to cluster growth, which leads to formation of small clusters.

4.1.2. Clusters, nanoparticles and large aggregates chemically generated on preformed polythiophenes

An alternative approach with respect to that just described consists in a chemical reduction of a suitable metal salt in the presence of a polymer matrix, previously synthesised either by chemical or by electrochemical procedures. As above discussed, the generation of metal inclusions occurs either on the surface or inside the polymer matrix. The preformed PTh film is immersed into a solution containing an Au(III) salt, i.e. AuCl_3 , leading to the insertion of AuCl_3 inside the polymeric film; then, the film is immersed into a solution containing NaBH_4 reductant, leading to the formation of Au NPs [248]. This procedure can be repeated and a progressive increase of NPs density is observed, at least on the surface of the film.

A similar procedure is not only suitable for the direct formation of the composite material on an electrode surface. Similar composite materials can be also synthesised in solution, through the reduction of HAuCl_4 by NaBH_4 in the presence of chemically synthesised poly(3-hexylthiophene), acting as the encapsulating agent [249]. The redox reaction between poly(3-hexylthiophene) and AuCl_4^- ions is prevented from occurring by using a large excess of tetraoctylammonium bromide (TOABr) in the reaction solution. The resulting composites result soluble in organic solvents; hence, films of this composite have been obtained by casting procedure.

By using an analogous synthetic approach, Pt and Pt-Ru NPs have been synthesised using a solution of PEDOT/PSS composite added with H_2PtCl_6 and RuCl_3 ; formaldehyde or hydrazine were then added, acting as reducing agents [238,250-253].

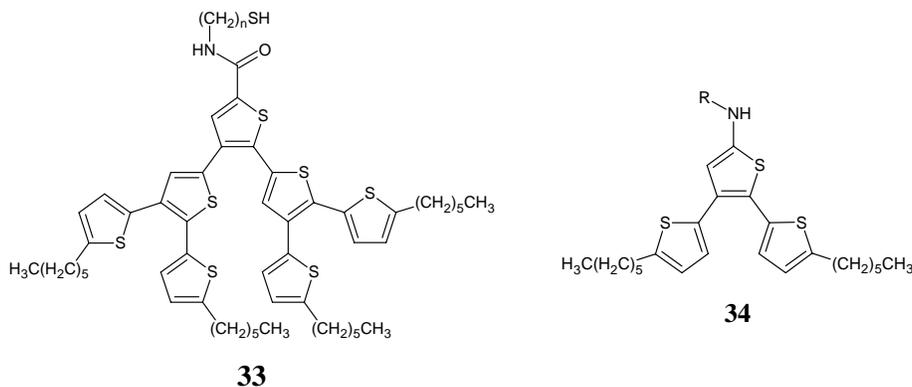
Alternatively, the Th backbone itself can undergo oxidation, acting as the reductant of the Au, Ag or Cu metal salt precursor; the process, often called electroless deposition, normally occurs both in solution [254] and on the PTh thin film deposited on an electrode surface [243,255,256]. The nature of the metal NPs can be changed through a galvanic exchange reaction. This process is based on the dissolution of the metal constituting the NPs and the contemporary deposition of a second metal, possessing a suitable reduction potential. These redox reactions have been employed for the deposition of Pd NPs on a PEDOT coating, previously modified with Cu NPs [243].

An alternative technique is based on the adsorption of a reducing agent, normally hypophosphite ions, on a substrate. The adsorption step is followed by a complex series of reactions leading to the oxidation of the hypophosphite ions and the contemporary reduction of metal ions present in solution. These redox reactions lead to the formation of small particles on the substrate, which act as 'seeds': the adsorption process and reduction reaction proceed on the surface of the particles, progressively increasing their size. This technique has been widely employed for the formation of coatings on metal substrates, e.g. Ni on steel [257]. A similar approach has been employed also for the deposition of Ni NPs on P3MT film [227]. In this case, hypophosphite ions can not be directly adsorbed on the surface of the polymer. Hence, it is mandatory to electrodeposit some Ni particles on the polymeric coating, in order to generate some seeds suitable for the adsorption of hypophosphite ions and for inducing the catalytic redox reaction previously described. The resulting NPs are not constituted solely of the metal, e.g. Ni, since a parasitic reaction leads to the formation of phosphorous trapped inside the NPs.

4.1.3. Adsorption of chemically prepared thiophene derivatives on nanoparticle surface

Different oligothiophene derivatives have been adsorbed on NP surface, forming soluble composites that have been deposited on different substrates. Branched oligothiophene dendrons bearing a thiol terminal group (compound 33) as the encapsulating agents in the synthesis of Au NPs have been prepared; tetrabutylammonium borohydride and didodecyldimethyl ammonium bromide were also added, acting as reducing and co-encapsulating agents, respectively [258]. Actually, the dendrons form SAMs around the Au cores, by exploiting the presence of the -SH group; in this case, the alkyl chain acts as the spacer and the dendrimeric Th molecule is the tail group. The resulting NPs are soluble in low polarity organic solvents, also thanks to the presence of an alkyl chain suitably bound to the Th rings. These composites have been deposited on mica and highly oriented pyrolytic graphite surfaces, through spin coating technique.

Another kind of composites based on dendrimers has been prepared using a fourth-generation poly(amidoamine) dendrimer terminated by compound 34 [259]. Cu, Pd and Au NPs have been generated introducing the corresponding metal ions into the dendrimeric structure; the metal ions have been subsequently chemically reduced. The resulting composites are soluble in organic solvents and stable at least for weeks. These composites have been deposited on highly oriented pyrolytic graphite surfaces through spin coating technique.



4.1.4. NP mixed with PTh

The polymeric matrix and the NPs can be synthesised independently, and then 'mixed together' in a suitable solvent. In this case, the polymeric matrix is usually prepared by chemical methods. Literature reports both the use of 3-alkylthiophene dissolved in organic solvents [260-264] and of PEDOT/PSS in water [265]. Au NPs encapsulated by TOABr [260,261] or decanethiol [262] and Ag NPs encapsulated by hexadecyl ammine [264] have been used. In addition, SiO₂ core-Au shell NPs have been used [263]. These nanostructures have been synthesised by modification of SiO₂ particles (120 or 340 nm diameter) with 3-aminopropyltriethoxysilane [265]. The outermost region of the resulting particles exposes -NH₂ groups, which anchor small Au NPs (1-2 nm diameter) to the SiO₂ surface. The size of the NPs is enlarged by means of the chemical reduction of HAuCl₄ on Au NPs surface, leading to the formation of a continuous Au shell, few tens of nm thick, on the surface of the SiO₂ core. The SiO₂ core-Au shell NPs seems not to be encapsulated.

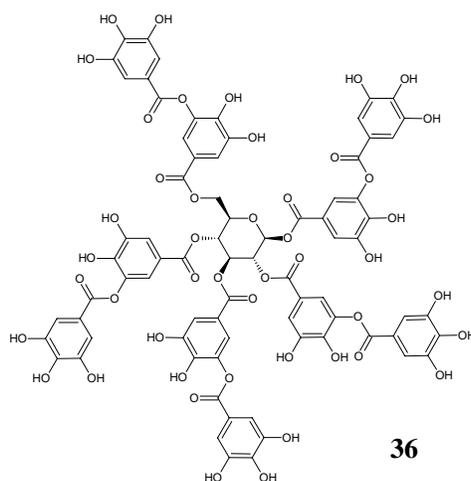
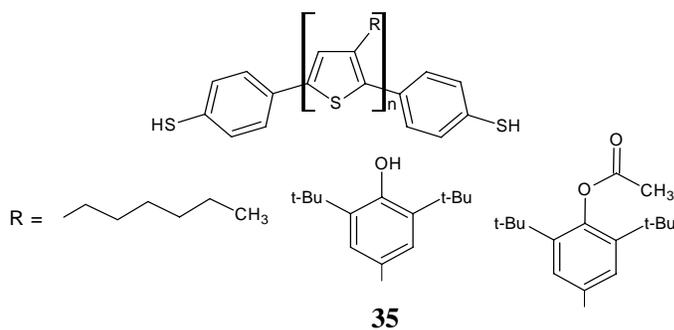
Although NPs may be trapped inside the polymeric matrix mainly by mere mechanical effect, the trapping process can be favoured by the presence of Th rings in the polymeric backbone, thanks to adsorption processes discussed previously. Embedding can also be favoured by the presence of anchoring groups bound to the polymeric backbone. These groups can be chemisorbed on the surface of the NP metal cores or can interact with the relevant encapsulating agent. As an example, thiol groups bound to the ends of a PTh backbone have been used for the formation of composites containing Au NPs encapsulated by a labile agent, namely TOABr [266]. In solution, the thiol groups substitute for the encapsulating species on the NP metal core, forming a bridge between adjacent metal cores. In addition, the Th units of the polymeric backbone have been functionalised in the β-position with hexyl chains, 3',5'-di-tert-butyl-4'-acetoxy-phenyl and 3',5'-di-tert-butyl-4'-hydroxy-phenyl moieties (compounds 35). The solubility and electrical conductivity of the composite are strongly dependent on the nature of the substituent. In particular, the 3',5'-di-tert-butyl-4'-hydroxy-phenyl moiety leads to the formation of an insoluble composite possessing very high conductivity, probably thanks to a particularly long effective conjugation and to formation of the phenoxyl radical.

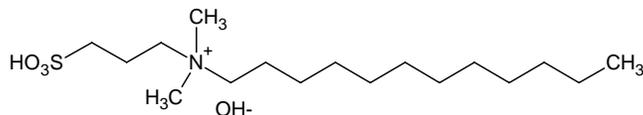
4.1.5. Electrogeneration of polythiophenes in the presence of nanoparticles

The electropolymerisation process can be performed in the presence of NPs, dissolved in solution together with the monomer and the supporting electrolyte. In this case, attention has to be paid to the experimental conditions chosen, in order to prevent from metal core aggregation eventually occurring in a solution characterised by high ionic strength, due to the necessary presence of the supporting electrolyte. In most cases the polymerisation is carried out in organic solvents [264,267-270]; though successfully employed [271,272], aqueous solutions have been more rarely used.

The encapsulating agent chosen is normally labile, in order to favour intimate contact between the NP core and the polymeric matrix. In particular, citrate ion has been used for the encapsulation of Pt and bimetallic Pt-Pd NPs, making the electrogeneration of the composite occur in CH₃CN [267]. Au NPs encapsulated by compounds 36 and 37 have been used for the preparation of PEDOT-based composites in aqueous media [271,272]. These encapsulating agents guarantee good solubility of the resulting NPs in water and stability of the NPs even in solution of high ionic strength, as conditioned by the presence of the supporting electrolyte.

Alternatively, the encapsulating agent used for the synthesis of the NPs can be the same monomer used for the electrogeneration of the polymer. As an example, EDOT has been used for playing both roles [264,268,273]. In this case, the arising polymeric chains are supposed to be in direct contact with the NP core, since the monomer adsorbed on the NP surface is also involved in the polymerisation process, becoming a unit of the PTh molecules that constitute the organic component of the deposit.

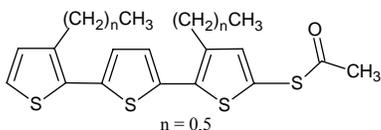
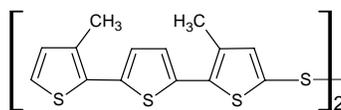
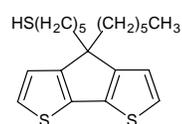


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Quite interestingly, NPs can be encapsulated by thiol molecules bearing a Th unit at the outermost end (see Figure 7). A SAM is formed ‘around’ the metal core, the Th residue constituting the relevant tail: the electropolymerisation leads to the formation of copolymer chains including the thienyl residue of the encapsulating agent. The NP core results connected to the polymer chains through the spacer and the head groups of the SAM. Literature reports the preparation of copolymers involving 3-butylthiophene [274], 3-hexylthiophene [269] and 3-octylthiophene [270]; the Au NPs were encapsulated by 5-(3-thienyl)-1-pentanethiol, 3-(11-mercapto-1-undecanoxyl)thiophene or 2-mercapto-3-octylthiophene, respectively.

Nanowires consisting of 3-butylthiophene copolymerised with the thienyl residue of 5-(3-thienyl)-1-pentanethiol encapsulating Au NPs have been obtained through the electrogeneration of the composite. In this case, the template employed for the growth of the nanowires is based on a porous alumina membrane adhering to a Au electrode [274].

However, literature also reports examples of polymerisation of thienyl residues, linked to NP metal cores, in the absence of other Th derivatives in solution. In this case, Au NPs have been encapsulated by a SAM consisting of a terthiophene bearing a diphenylphosphine group in one α -position; it constitutes the head of SAM [209,275], anchoring the Au core, while the terthiophene moiety constitutes the spacer and the tail of the SAM, at the same time. The electropolymerisation leads to the formation of oligothiophene chains forming bridges between adjacent metal cores, even connecting more than two cores. Au NPs encapsulated by compounds 38, 39 and 40 have been polymerised both chemically, using iodine as the oxidant, and electrochemically. The resulting hexamer or polymer form bridges between adjacent metal cores [210]. Once more, the bridges most probably connect more than two cores.

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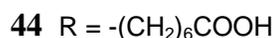
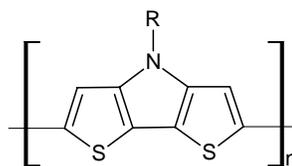
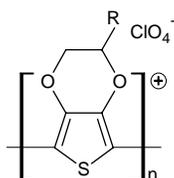
Alternatively, Au NPs encapsulated by a SAM based on 3-(10-mercaptodecyl)thiophene have been synthesised [276]; the thiol moiety constitutes the head group and the Th ring is the tail group. The addition of an oxidant, e.g. FeCl_3 , to a dilute solution of NPs leads to polymerisation of the tail groups of the same encapsulating cloud; the concentration of Au NPs, in fact, is low enough to prevent inter-particle polymerisation.

4.1.6. Nanoparticles adsorbed on preformed polythiophenes

The procedure consists first in the formation of a PTh film on a substrate; then, the system is put in contact with a solution containing NPs. NPs anchor the polymer surface or

even enter the film more or less deeply, depending on the porosity of the organic matrix, on the nature of the solvent and of the NPs and relevant encapsulating agent. Examples concerning Au and Ag NPs anchored to P3MT [277] or to PEDOT [277,278] films have been reported.

Nafion[®] can be strongly adsorbed on conductive indium tin oxides (ITO) slides, leading to negatively charged substrates, capable to anchor positively charged PTh derivatives. In particular, PEDOT-dodecylbenzene sulphonate, as well as compounds 41 and 42, have been deposited from the relevant solutions [278]. In addition, electrogenerated PEDOT, as well as compounds 43 and 44, have been deposited directly onto ITO [278]. As a final step, Au NPs encapsulated by TOABr have been anchored to the different polymeric films, thanks to a place exchange reaction between TOABr and PTh derivatives.

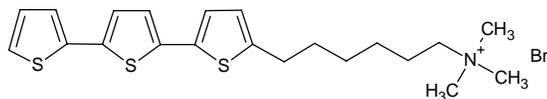


4.1.7. Simultaneous formation of polythiophene matrix and nanoparticles

The method consists of the simultaneous formation of the PTh matrix and of NPs: metal ions are reduced by the Th monomers, which are in turn oxidized to lead to the polymer. It is worth noticing that the chemical polymerisation of Th derivatives is normally carried out using FeCl_3 as the oxidising agent. Literature reports the synthesis of PTh-Au NPs composites starting from an aqueous solution of Th added with a solution of HAuCl_4 in dilute HCl [279]. The reaction leads to the formation of a suspension consisting of a PTh particles embedding Au NPs, and of a dark precipitate containing PTh and Au. Alternatively, EDOT is dissolved in water and an aqueous solution of HAuCl_4 is added, leading to the formation of PEDOT embedding Au NPs [280]. The addition to the reaction mixture of species such as cetyltrimethylammonium bromide, sodium dodecylsulfate, polyvinylpyrrolidone and PSS, strongly influences the nature of the composite. In particular, the use of PSS leads to a water soluble nanocomposite, whose aqueous solutions are stable also at high ionic strength. The reaction can be also carried out in the presence of different alkylamines in THF [281]. The nature of the alkylamine strongly influences the aggregation of the NPs, although a rationale to this fact is still absent. In addition, composites containing Cu NPs have been synthesised starting from EDOT and CuCl_2 ethanolic solution [282]; a redox reaction similar to that involving AuCl_4^- and monomers leads to the formation of Cu NPs and of PEDOT.

Other authors proposed the formation of Au NPs from HAuCl_4 in the presence of compound 45 [283]; the resulting oxidation leads to the formation of the relevant hexamer, at least at high trimer concentration. In order to increase the solubility of compound 45, NaPSS

surfactant has been added to the solution. The formation of a strong ionic couple between compound 45 and PSS is envisioned.

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A similar redox reaction can be also photo-induced. By exploiting this synthetic approach, Ag NPs have been prepared by irradiating a solution containing Th and AgNO₃ with UV light (365 nm) for three days [284]. The resulting composite consists of Ag metal cores surrounded by a thick layer of materials (<75 nm) whose nature is not clear; in particular, Ag⁺ ions are supposedly present.

4.1.8. Surface polymerisation

The synthetic approach reported in Section 4.1.7 has been adopted also to perform contemporary polymerisation and metal salt reduction directly on the surface of a substrate. In this case, a suitably functionalised substrate is put in contact with a solution of the oxidant, normally a metal salt, which leads to the deposition of the oxidant on the substrate. Then, the ‘activated’ substrate is exposed to vapours of a Th monomer. The metal ions on the substrate are reduced to metal NPs and the monomer is converted into the relevant polymer, which forms a thin film on the substrate, incorporating the NPs. As an example, polyethylene terephthalate substrate has been treated with a solution of CuCl₂ by spin coating method; the thin layer of oxidant solution has been exposed to EDOT vapours, leading to the evaporation of the solvent and the contemporary formation of Cu NPs and nanorods on PEDOT film [282].

The ‘opposite’ process has also been proposed. The Th monomer has been deposited onto the substrate; then, the modified substrate has been exposed to a solution of the oxidant, leading to the formation of the polymer. As an example, Au NPs have been prepared depositing a solution of 2,5-di(thiophen-2-yl)-1H-pyrrole mixed with a second polymer, such as polystyrene-block-poly(2-vinylpyridine), poly(2-vinylpyridine) or poly(4-vinylpyridine) on a glass substrate by spin coating [285]. Finally, the modified substrate has been dipped in a solution containing HAuCl₄, leading to the formation of Au NPs.

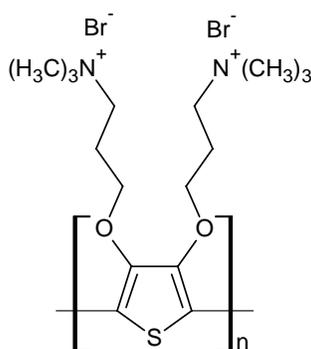
4.1.9. Layer-by-Layer deposition

Typically, Layer-by-Layer deposition technique (LbL) constitutes quite a common procedure for building up multilayers consisting of alternating cationic and anionic polyelectrolytes (PE) [286]. The formation and stability of the composite are ascribed to multiple electrostatic interactions between layers possessing opposite charges. The growth of the multilayer is generally performed by simply dipping the bare substrate into a solution containing a charged first component; after suitable washing, the second layer is deposited by dipping the modified substrate into a solution containing an oppositely charged component, and so on. The deposition of each additional layer leads to surface charge reversal, i.e. the charge present on the substrate is overcompensated after the deposition of an additional layer.

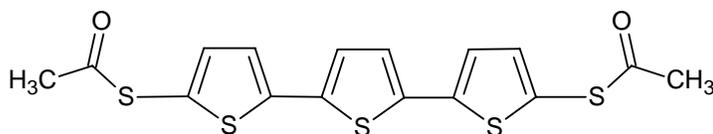
The stability of the multilayer system allows one to repeat the procedure even many times, leading to a control of the thickness, with nanometric resolution, in the 1-100 nm range. Moreover, the multilayer fabrication is easily automated, due to the experimental simplicity and the high reproducibility of the method. The substrate surface should possess a net charge in order to allow the anchoring of the first layer of charged component. The charge can be conferred by anchoring suitable molecules; as an example, thiol molecules bearing an ion group in ω -position with respect to the SH group have been employed.

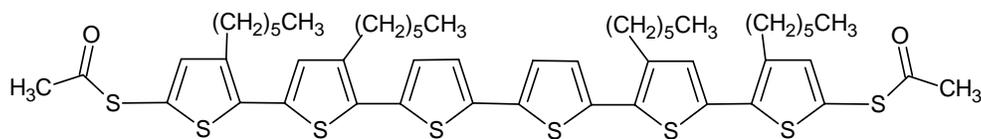
LbL procedures can be also followed for the development of PTh-NP composites. In a first example reported [229], a poly(4-vinylpyridine) N-functionalised with terthiophene groups has been employed as the cationic polyelectrolyte of the multilayer and polyacrylate constitutes the anionic counterpart. The multilayer has been immersed in a solution of HAuCl_4 , leading to the formation of Au NPs and to the contemporary oxidation of the terthiophene moiety to the relevant hexamer. The deposition has been carried out on different substrates (glass, quartz, Si), previously modified with poly(ethylenimine), i.e. exposing a NH_2 -modified surface.

Alternatively, LbL deposition procedure was also exploited for the deposition of pre-formed NPs. In this case, a multilayer based on compound 46, i.e. a cationic PTh, and anionic Au NPs encapsulated by 11-mercaptoundecanoate has been deposited onto different substrates, such as glass, ITO, Au, Si(100) wafers [287]. Glass, ITO and Si(100) wafers have been modified with 3-aminopropylethoxysilane and treated with aqueous acid solution, leading to substrates which expose $-\text{NH}_3^+$ groups.

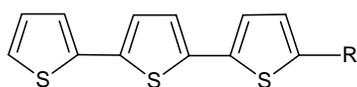
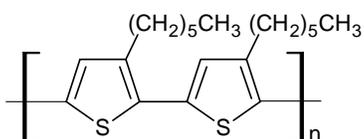


As a further example of LbL deposition, however not implying subsequent layer interacting electrostatically with each other, a Au substrate has been dipped alternatively in a solution containing Au NPs encapsulated by TOABr and in a solution of a Th-based derivative. The derivatives used are oligomers bearing two groups in correspondence of the α -positions at end of the chain. These groups are designed in order to be adsorbed on Au NP core surface. In particular, molecules such as 47 and 48 [210] have been used.

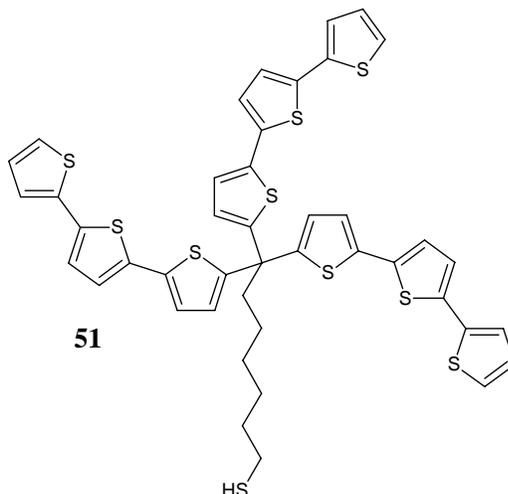




48

49 R = $-(\text{CH}_2)_6\text{PO}_2\text{H}_3$ 50 R = $-(\text{CH}_2)_6\text{SH}$ 

52



51

Alternatively, ITO surfaces have been functionalised with 3-mercaptopropyl-trimethoxysilane (MTS) or compound 49 [288,289]. The modified substrates have been dipped in a solution containing Au NPs encapsulated by TOABr, leading to the anchoring of a monolayer of NPs. The resulting modified substrates have been alternatively dipped in solutions containing compound 50 or 51 and Au NPs. A modified procedure is based on the deposition of compound 51 followed by its electrochemical oxidation to the relevant hexamer [288].

Finally, Th-based polymers, β -functionalised with suitable side chains in order to anchor NP metal cores, have been synthesised. As an example, multilayer based on compound 52 and Au NPs encapsulated by TOABr have been deposited on, e.g., Au [210]; the tetraalkylammonium salt is supposed to be at least partially substituted by the thiol groups and, perhaps, by the Th backbone.

4.1.10. Langmuir-Blodgett and Langmuir-Schaeffer films

Langmuir-Blodgett (LB) and Langmuir-Schaeffer (LS) techniques constitute well known procedures for preparation of thin films of molecules on a solid substrate [290]. These techniques enable the homogeneous deposition of the thin layers over large areas, the control of the thickness of the layers, and the obtainment of multilayer structures by even varying the composition of subsequent layers. The apparatus for the deposition of LB and LS films is composed by a suitable tank filled with a solvent, normally water, called subphase. The molecules to be deposited are dissolved in a solvent immiscible with the subphase. This solution is spread over the subphase; after the evaporation of the solvent the molecules form a very thin layer on the subphase. This layer can be transferred to a substrate by dipping the

substrate in the subphase: in the case of LB deposition, the substrate surface is dipped orthogonally with respect to the subphase, while in the LS technique the substrate surface is coplanar with the subphase.

LB and LS are widely diffused techniques for the deposition of CPs on different surfaces [291-294]. At present, polymeric LB and LS films are obtained by three main methods: *i*) by forming polymer monolayers on the surface of a liquid and transferring them to a solid substrate; *ii*) by forming monomer monolayers on the subphase, polymerising them, and transferring the obtained polymer to a solid substrate; *iii*) by forming LB or LS films of the monomer on the substrate and performing polymerisation after removal of the substrate from the subphase. It is important to point out that it is possible to obtain different structural organisation for LB or LS films possessing identical chemical compositions, though obtained by following different procedures.

Few examples of PTh-NP composites prepared by these techniques have been reported. It is worth noticing that the deposition of PTh-NP composites can lead to PTh possessing a certain degree of order, as pointed out in some papers [295,296]. The highest degree of order is normally obtained using regioregular PThs.

As to the literature reports, an organic solution of Au NPs capped with a SAM of dodecanethiol molecules has been spread on a water surface, forming a hydrophobic film [297]. The Au NPs has been deposited onto a SiO₂ surface by means of LB technique, forming a very fragile film, soluble in organic solvents. Then, the modified substrate has been dipped in a dilute solution of compound 47. A partial displacement reaction takes place, leading to the formation of bridges between Au metal cores. Each layer, after treatment with the terthiophene derivative, is ca. 3.5 nm thick. The formation of bridges increases the stability of the film with respect to mechanical stresses and the action of organic solvents; moreover, the electrical conductivity of the film is increased.

Alternatively, a blend composed by poly(3-hexylthiophene) and Au NPs encapsulated by dodecanethiol has been spread over water and deposited onto glass slides, previously modified by hexamethyldisiloxane in order to obtain an hydrophobic surface [295,296]. In this case the LS technique has been used and film thickness up to ca. 10 nm has been obtained.

5. POLYTHIOPHENES AND METAL OXIDES

The synthesis of a variety of composites consisting of CPs and metal oxides has been the focus of intense research [28-30]. Based on the nature of association between the inorganic and organic components, we can distinguish *i*) the so-called inorganic-in-organic composites, where the metal oxide NPs are embedded in an organic matrix and *ii*) the so-called organic-in-inorganic composites, where the organic polymer is confined inside metal oxide templates [28]. These composite materials are mainly characterised by photoactive (both photoelectrocatalytic and photoelectrochromic), capacitive, charge storage and electrocatalytic properties, finding applications in charge and energy storage devices (batteries and solar cells) and, even if to a less extent, in sensors.

The introduction of molecular inorganic species into a CP network can be conveniently accomplished by taking advantage of the doping process of the polymer, leading to the

incorporation of charge balancing species into the organic structure. Following this synthetic route, an interesting example of inorganic-in-organic polymer-metal oxide composites is obtained using polyoxometallates (POMs) [298]. POMs constitute a large family of negatively charged clusters formed by a predominant transition metal (usually W or Mo) framework and oxide anions, mostly known for their catalytic properties. POMs not only share structural and topological features with related transition metal oxides, but also resemble them with respect to redox, electron transfer, and ion transport behaviour. The well-defined structure, the characteristics of undergoing reversible multi-electron charge transfers, and the unique photoelectrochemical properties of these nanosized model oxide particles make them attractive for many applications as electrode materials for energy storage devices. Composite materials containing POMs can be synthesized by entrapping, within the framework of the polymer, bulky anions from heteropolyacids, thanks to electrostatic interactions. The permanence of the anions inside the polymer matrix upon reduction forces the insertion of cations in order to ensure charge balance. The inverse process of cation expulsion takes place upon re-oxidation, thus converting p-doped polymers into redox material capable to insert cations. The composite material possesses all the unique properties of the CPs, summed to the activity of the entrapped inorganic species, which remain stably anchored inside the polymer. The most commonly studied CPs in the frame of POMs composites are polypyrrole and polyaniline, which can undergo fast degradation processes during repeated charge-discharge cycles, such as in applications to supercapacitors. In this context, an alternative and efficient CP is represented by PEDOT and PEDOT derivatives, which are even commercially available.

The composite material can be also synthesised by simply mixing the monomer with an excess of heteropolyanion, that also acts as the oxidant, initiating and prosecuting the polymerisation process. This chemical synthesis is usually chosen for applications in supercapacitors, since a high amount of material is obtained in a short time. Sometimes, however, a low degree of cross-linking, and then a higher degree of solubility of the resulting composite, is obtained; in these cases, an external oxidant has to be used [299]: H_2O_2 is an ideal candidate, since one of the goals of the synthetic procedure lies in anchoring the maximum amount of electroactive POM, possibly avoiding the insertion of other anions that can compete with POMs in the compensation of the positive charges on the polymer backbone. An alternative way to reach this goal is to perform electrochemical synthesis. Moreover, polyanions such as POMs are particularly suitable for the electrodeposition of some PThs such as PEDOT [300,301], since it is known that anionic surfactants in aqueous media improve the monomer solubility and facilitates electrosynthesis [302,303]. In order to obtain multilayered organised assemblies of PEDOT-POMs with well-defined composition, structure and thickness, the LbL technique has also been employed [304,305]. In this case, the electrode substrate is firstly modified with a self assembled POM monolayer by dipping it in an aqueous solution of the relevant heteropolyacid. Then, the modified electrode is immersed in acid solution containing the EDOT monomer, which is supposed to be under cationic form in this medium, and thus attracted by the POM layer. The following polymerisation step is performed electrochemically, by cycling the electrode potential over a suitable potential range. By repeated and alternate treatments in the appropriate solutions, the amount of material on the electrode surface can be increased in a controlled way. The LbL procedure has also been efficiently used to fabricate composites with improved electrocatalytic properties, consisting in layers of Pt NPs [304], carbon NPs [305] or carbon nanotubes [305]

encapsulated by negatively charged POMs, electrostatically attracted by ultrathin layers of positively charged PEDOT [305]. The procedure is very similar to that previously described, with the only difference that in the first step the electrode is dipped in a suspension of NPs or nanotubes stabilised by POMs. Consequently, the attractive mechanical and electrical characteristics of nanostructured carbon, the unique properties of CPs and the reactivity of POMs are combined. On the whole, the functionalisation of metal NPs or of carbon nanostructures with heteropolyanions constitutes an effective route to their homogeneous dispersion in polymeric matrices. The resulting films are characterised by fast charge transport, assuming potential importance to electrocatalysis and charge storage in redox capacitors.

Other composites prepared by exploiting the doping process of CPs are represented by organic-in-inorganic materials, comprising conductive organic polymers interleaved between layers of an inorganic oxide lattice such as V_2O_5 or MoO_3 powder. The redox active nature of both components offers promising possibilities in such electrochemical applications as positive electrode materials in lithium ion batteries. The large, immobile, inorganic matrix represents a component which both acts as the counter anion of the CP and participates to the redox processes. In this way the anion exchange, which is the primary charge compensation phenomenon occurring during discharge process of the CP, is suppressed, and lithium ions insertion is favoured. On the other hand, the CP can in principle improve the electron transport properties and even enhance the ionic diffusion efficiency inside the transition metal oxide matrix, by minimising steric and electrostatic limitations to lithium transport within the oxide host. Polymeric intercalants such as polyaniline presents certain limitations, such as the possible presence of benzidine moieties in the polymer backbone that might yield toxic products upon degradation. For this reason, composites based on Th monomer, which are known to be more eco-friendly systems, have attracted the attention; they undergo oxidative polymerisation when intercalated to highly oxidising materials such as V_2O_5 . In particular, the use of Th derivatives as starting materials allowed the *in situ* polymerisation by the inorganic host [306]. Murugan et al. studied the effect of changing the crystalline oxides (MoO_3 , MoS_2 , V_2O_5 , VS_2) and the polymerization conditions of PEDOT production on the properties of the resulting composite [307-313]. The composite formation can be performed by a process consisting in refluxing an aqueous solution containing the monomer, an oxidising agent and a suspension of the metal oxide powder [306,307,309,311]. This procedure often comprises several steps and takes long time, so that alternative methods have been developed. In particular, the microwave-assisted method assures cleanliness, short reaction times, energy economy and structural uniformity of the product formation [308,310,312,313]. In this case, the reaction mixture is exposed to microwave radiations causing hydrothermal heating. The selection of microwave irradiation plays a key role in significantly reducing the time for preparation (some minutes), compared to that of conventional preparative methods (several hours). In a recent paper [314], the formation of a bilayer of WO_3 and PEDOT has been proposed as an efficient tool to improve charge transfer, redox activity, electrochemical stability and also colouring efficiency, with respect to the neat polymer film. The bilayer was synthesised by first forming a WO_3 layer by surfactant-assisted electrochemical method on an ITO substrate, followed by spin-coating deposition of a PEDOT/PSS layer.

CP-Metal oxide composites can also be formed embedding metal oxide NPs in the organic matrix. This kind of composites of CPs and semiconductor oxide NPs are subject of intense investigation due to their wide application in electronic and optoelectronic devices.

Most CPs have a band-gap well matched to the visible-light range and suitable for photovoltaic devices, but suffer from low charge mobility and short excitation diffusion length. Semiconductor nanocrystals offer a potential solution to these deficiencies, since they can be mixed with the CP to form heterojunctions. Normally, the NPs serve as electron acceptors, due to their higher electron affinity, while the polymer acts as the electron donor. Among CPs, PTh derivatives are particularly suitable materials for applications in organic solar cells, since they are chemically stable in ambient conditions and can form good electric contacts with metal electrodes. The composite can be formed by simply mixing a soluble PTh with colloidal TiO₂ powder; then, drop casting deposition of the resulting solution onto the substrate is well effective [315]. In alternative, chemical polymerisation, typically using FeCl₃, after adsorption of Th monomers onto metal oxide powder, represents a simple and fast method applicable to a variety of oxide particles of different grain size and to various Th derivatives, both in organic and in aqueous media [316-319]. A similar procedure was adopted to introduce TiO₂ nanotubes into PTh [320].

In order to anchor on conductive surfaces thin composite layers of metal oxide NPs covered by a PTh thin layer, the electrophoretic deposition method has been employed [318,321,322]. The core-shell system is prepared by adding FeCl₃ to a solution containing Th and dispersed metal oxide NPs. The resulting NPs, dispersed in a proper solvent, migrate under an electric field, and then coagulate onto the electrode surface forming a homogeneous nanostructured deposit.

Metal oxide NPs can also be inserted after polymerisation to PTh. For example, RuO₂ particles have been incorporated into PEDOT/PSS matrix to form an electrode material for electrochromic pseudo-capacitors [323]. PEDOT/PSS films can be prepared using spin coating technique or electropolymerisation; then, RuO₂ particles can be inserted electrochemically by repeated cyclic voltammetric scans in a solution containing a pristine ruthenium salt, or using the dipping-hydrolysis method [323,324]. According to this last approach, the PEDOT-covered electrode is dipped in aqueous RuCl₃ solution; air pressure and suction are applied alternately over the solution, so that the solution soaks into the pores on the polymer surface. Then, the polymer with loaded Ru salt is treated with NaOH to hydrolyze the Ru salt.

Finally, ultrathin films of PTh-SnO₂ composite were used for gas detection via conductivity measurements [325]. The composite films were fabricated by self-assembly technique. The CHCl₃ solution of PTh was spread at the air/water interface containing SnO₂ particles and was kept 1 hour to absorb the NPs. Evaporation of CHCl₃ left a thin film of composite that was lifted horizontally from the surface of water and transferred to the substrate.

6. CHARACTERISATION OF THE HYBRID/COMPOSITE MATERIALS

6.1. Electrochemistry

Electrochemistry plays a major role in the preparation and characterisation of PTh-based materials, especially in the frame of electrochemical systems. On the one hand, electrochemical techniques are especially suitable for carrying out syntheses under controlled

conditions and for tuning a well-defined oxidation state. On the other hand, obviously, electrochemical characterisation of the resulting material, either purely organic or containing the inorganic component, represents the way to obtain information about the (electrochemical) properties of the material, which is often the main goal for the kind of systems we are dealing with in this survey. Among these properties, the definition of the potential range over which it is conductive is a preliminary one.

Direct electrochemical synthetic procedures can often be used whenever the composite or hybrid material forms concurrently to the polymer. In these cases an electrochemical approach permits the control of the actual film formation and deposition. In particular, when the growth is carried out under potentiodynamic conditions, e.g. by cyclic voltammetry (CV), the success of the synthesis on the electrode substrate is evidenced by the progressive increase of the peak currents due to polymer doping and de-doping. If the hybrid or composite material contains redox active species, such as metal ions or POMs [300], a regular increase of the relevant peak systems can be also observed, which is a check of a fairly homogeneous distribution of the metal centres within the film. This approach is frequently adopted in the case of metallopolymers, so that cyclic voltammograms referred to electropolymerisation are almost always reported in the literature. It should be underlined that the electrochemical synthesis may be critical when metal ions are electronically connected to the polymer π -system: the actual formation of a conductive PTh based materials can be quite difficult [45,51,53-58,68-70,100,101,108,142,146].

In principle, a number of information can be obtained by the electrochemical characterisation of the electrode coating, performed in a solution only containing the supporting electrolyte. Actually, caution should be used in drawing out reliable conclusions from the analysis of the responses. They result, in fact, from many 'in parallel' and 'in series' steps [2] that include, at least: *i*) the faradic process (generation, near the electrode surface, of charges on the polymer chains); *ii*) the percolation of charges through the film, by intra- and inter-chain electronic conduction, eventually even by electron-hopping between adjacent metal centres; *iii*) the ion exchange at the film|solution interface, in order to preserve electroneutrality of the coating, as realised by *iv*) the migration, rather than diffusion, of counterions and/or co-ions within the polymer bulk. In parallel, more or less deep structural modifications of the polymer film progressively occur, which continuously modify the characteristics of the deposit. That is why a correct examination of the current *vs.* time or current *vs.* potential curves is very often far from being accounted for by 'simple' models, based on equivalent circuit analysis, on purely analytical, semi-numerical, or on fully numerical simulation techniques. Although the interpretation of the voltammetric responses may be even more difficult in the presence of an electroactive inorganic component, this can lead to responses diagnostic of the actual formation of the hybrid/composite materials. As an example, in the case of metal PTh-NP composites, the presence of Au NPs has been testified by the current peaks ascribed to oxidation/reduction of the metal cores [326]. On the other hand, the presence of Pt NPs has been indirectly verified observing the peaks ascribed to hydrogen adsorption and desorption [252] and to hydrogen evolution [252].

By considering the voltammetric systems attributable to the organic component, the *i vs. E* curve recorded in CV tests is usually characterised by broad peaks, both in the forward (charging) and in the backward (discharging) scans. This is due to *i*) the wide

molecular weight distribution of the polymer chains; *ii*) the conformational and structural changes occurring for subsequent injections of charges; *iii*) the occurrence of polaron and bipolaron formation at potentials often relatively close to each other. The intensity, shape and position of the current signals due to the organic and inorganic components can give information about the film composition and about the actual electronic interaction between the two components. By considering the first aspect, the estimation of the film composition has been attempted, both the organic and the inorganic species being electroactive and the electronicity of the two processes being known, on the basis of the peak integrals of the two components [60,114]. For this purpose, as an additional strong request, the two oxidation peaks have to be well resolved. Once more underlying the risk of pretending reliable information from CV tests, it is evident that the occurrence of all conditions requested represents a very rare situation.

When considering the position and shape of the voltammetric peaks, the interaction among neighboring metal centres, especially in the case of metallopolymers, can result in some differences of the voltammetric trace with respect to the mere sum of the inorganic and organic contributions. In many cases, the peak ascribed to polymer p-doping results significantly shifted, due to a certain degree of stabilisation/destabilisation of either the conducting or the valence bands. Several examples are reported in Refs. 44, 51 and 67. By considering the peaks ascribable to the inorganic component, an electronic interaction with the polymer π -system can induce stabilisation/destabilisation of either HOMO or LUMO orbitals of the metal complex, together with broadening of the redox peaks due to different energetic effects on different metal centres [147].

Electrochemical investigations have also focused on the dependence of the peak height on the potential scan rates in CV tests [56,62,95,107], aimed at defining the character of the charging/discharging processes. Actually, this constitutes a very difficult task, due to the arguments discussed above.

On the other hand, in an operative context, CV experiments can constitute efficient tools to diagnose the stability of the hybrid or composite deposits. The eventual peak current decrease observed by subjecting the system to long-term CV cycling can originate from dissolution or from structural degradation of the composite material [100,142].

6.2. UV-Vis-NIR Spectroscopy

UV-Vis spectroscopy is a very powerful tool to draw out many useful information about the material, especially by comparing the behaviour of the hybrid or composite material to that of the pure organic component. In particular, the UV-Vis spectrum of a neutral PTh is characterised by one absorption band due to π - π^* transition; the relevant λ_{max} is related to the polymer conjugation length, while a more proper estimation of the polymer band gap is generally made on the basis of the onset of the band at higher wavelengths. In this case, the actual occurrence of an oligomerisation/polymerisation process can be directly verified by comparing the spectra of the resulting material with that of the relevant monomer

[47,62,119,152,208]. Furthermore, the presence of the inorganic component inside the film can strongly affect the location of the π - π^* absorption bands [46,51,52,60,71,74,143,154]. Two main causes account for this effect: *i*) the presence of the inorganic component during polymer electrogeneration process may affect the length of the resulting polymer chains, which generally result shorter, as deduced by hypsochromic shift of the π - π^* absorption band; *ii*) electronic interactions between the organic and the inorganic components may induce electronic stabilisation or destabilisation of the conduction and/or valence band of the polymer.

When undergone to a p- or n-doping process, a PTh film leads to record characteristic spectra. In particular, the formation of polarons is evidenced by two absorption bands in the Vis-NIR range, while the spectrum evolves to only one absorption, located between the two bands typical of the polaron, when the bipolaron is the main species present inside the film [327-329]. With this respect, *spectroelectrochemical* experiments, i.e. spectroscopic characterisations performed by polarising the electrode at different applied potentials, afford useful information regarding the polymer charge and discharge processes. In this case, a comparison of the spectra recorded for the hybrid or composite material with those relative to the merely organic one can give suggestions about the effect of the inorganic component on the properties of the material. This aspect is particularly important when the interpretation of the voltammetric trace, i.e. the attribution of each electrochemical process to a specific peak system, is not straightforward [79,80,154,272].

Analogously to what discussed in the case of the electrochemical characterisation, also the interpretation of the UV-Vis spectra can become quite difficult if also the inorganic component shows absorption bands in the same spectral region. On the other hand, the inclusion of inorganic species showing typical absorption bands can be exploited in order to gain a direct proof of the presence of the inorganic component inside the material [45,46,51].

Particularly useful information are collected in the case of NPs included inside a polymer film. In metal NPs, in fact, 'free' electrons are trapped in the metal cores. An incident radiation at suitable wavelength generates a collective oscillation of the electrons, leading to the formation of instantaneous dipoles [330]. This phenomenon can be evidenced in the UV-Vis absorption spectra, typically in the case of Cu, Ag and Au NPs: a broad peak, called *surface plasmon band*, is present. As an example, the red colour of Au NP solutions is due to this absorption, whose band is located at ca. 500-530 nm. A general theory explaining this behaviour was developed by Mie [331]. The intensity, width and exact position of the band are dependent on a large number of parameters, such as the size and shape of the NPs, as well as the temperature. Moreover, the dielectric constant of the medium in which the NPs are dispersed plays a crucial role. With this respect, in the case of PTh-NP composites, the presence either of the encapsulating agent or of the PTh matrix in immediate contact with the NP, implies strong variation of the dielectric constant value, leading to significant variation in the general electronic properties of the NP and, in particular, in the plasmon band location [281]. Just based on the plasmon band location, some authors have proposed a way to calculate the mean size of the NPs [264]. A change in the position of the plasmon band has been also observed at varying the distance between the NPs [330]. The induced dipoles in each NP, in fact, are essentially independent of the distance between adjacent NPs only when they are far enough from one another. However, a reduction of the distance causes dipole-dipole interaction, with a corresponding red shift of the plasmon band. A further decrease of

the distance leads to the formation of conductive bridges between the metal cores, which in turn leads to the formation of additional dipoles and even quadrupoles [332]: the resulting UV-Vis spectrum exhibits two bands. A significant red shift of the plasmon band can also be observed when the NPs are relatively far from one another, but a conductive pathway along the metal core ensemble is present: in the case of PTh-NP composites, this pathway can involve the PTh molecules [32]. The extent of the red shift of the plasmon band has been widely exploited in the study of the NP aggregation phenomena eventually occurring both in solution and in the frame of NP systems anchored at surfaces; in the latter case aggregation may be induced by the deposition procedures of PTh-NP composites.

The arising of a plasmon band has been exploited also to check and follow the progressive formation of the NPs inside the polymeric matrix [229,280] or the presence of Au NPs inside the preformed composites [249,258,283]. It is obvious that, for similar studies, the composite must be either soluble or deposited on transparent substrates. By exploiting analogous approaches, the growth of composites through LbL technique has been followed by recording UV-Vis spectra after the deposition of each layer [210,287-289]: the spectra generally show the progressive increase of bands ascribed to the PTh matrix and to the plasmon oscillations.

6.3. Electrical Conductivity Measurements

The presence of metal species inside a PTh is reported to affect the electrical conductivity of the composite with respect to the pure organic material.

The measurement of the conductivity of thin films of PTh-based hybrid or composites is not straightforward. A sample is built, consisting of a pellet of the material under investigation, of a thin film deposited on a substrate, or even of a free standing film. The approach often followed for performing the measurement is based on four-point probes [210,217,238,248,249,252,278,288,319]: these are *ex-situ* measurements, carried out on dry samples. On the other hand, when using two-bands or interdigitated array electrodes [44,59,60,67,82,95,97,105,147,148,154,297,319], the measurement may be directly performed inside a solution only containing the supporting electrolyte, by polarising the modified electrode at chosen potentials, i.e. under strict control of the doping degree of the CP; in this case, the technique measures the *in-situ* conductivity [333]. Similar measurements are particularly useful also in the case of metallopolymers, because the shape of the conductivity *vs.* E curve gives useful information about the charge transfer mechanism occurring inside the film. In particular, in accordance to the studies performed by Zotti et al. [147,148], the presence of a bell-shaped conductivity *vs.* potential trace indicates that the charge percolation occurs through an electron-hopping mechanism between adjacent redox centres; on the contrary, a charge transport only ascribed to polarons and bipolarons results in a sigmoidal curve.

AFM can be used for the determination of the local conductivity of the NP-PTh composite surface [264,277,288]. Also in this case, the data reported suffer from being relative to dry material, in air atmosphere, which are not often the conditions in which the system is thought to work. Recently, Scanning ElectroChemical Microscopy (SECM) has been successfully employed for measuring the local electrical conductivity [295,296]. The

advantages of this technique consist in the possibility to work in liquids, even controlling the potential applied to the material under investigation.

6.4. Electrochemical Impedance Spectroscopy

When applied to CP modified electrodes, electrochemical impedance spectroscopy (EIS) has proved to be quite a useful tool for studying the charge transport inside the polymer coating, as well as the electron transfer at the metal/polymer and the ion transfer at the polymer/solution interfaces. However, several problems concern both the correct execution of the measurements and the interpretation of the data obtained, due to the high complexity of the system [2].

Numerous models have been proposed for the elaboration of EIS data obtained for CPs modified electrodes. One of the most diffused schemes simulates the charge-discharge process by a generalised transmission line circuit, which also offers the advantage of possibly ascribing a physical meaning to the results obtained [2,334,366-368]. When a fitting procedure is possible, double layer capacitance, ionic resistance, electronic resistance and diffusion coefficients can be computed.

The presence of metal centres inside a CP can cause more or less marked variations in the impedance plots with respect to that of the CP alone. A comparison between the impedance plots obtained at varying some experimental conditions, such as the applied potential, can help better understand the contributions of all the components to the electrochemical properties of the composite material [68,95,102,252,317,324]. This is, for example, the case of the PTh composites specifically designed for electrochemical capacitors, in which a variation of the Nyquist plot in the low frequency region, with the appearance of an almost 90° line (capacitive behaviour) and the disappearance of 45° slope line (diffusive behaviour), gives an immediate evidence of the enhanced capacitive character of the composite [324]. EIS has been applied also to calculate ionic conductivities for PEDOT/PSS supporting Pt NPs, at varying the metal loading [252].

In the case of metallopolymers, EIS has revealed to be important to study the quite complicated electron transport mechanisms and even to evaluate the electron transport rates. The occurrence of the superexchange charge transfer mechanism inside the polymer film obtained from compound 13 has been studied by EIS measurements, by calculating 'diffusion coefficients' for the electron hopping between metal sites [102]. Analogously, EIS has been used to define the potential range in which electron hopping is the rate limiting step for charge transport in metallopolymer film deriving from compound 11 [95]; close to the formal potential of the metal redox couple, ionic and electronic resistances are of the same order of magnitude and both ion migration and electron hopping contribute to the charge transport dynamics. Similarly, the EIS data of a Type I metallopolymers containing bipyridine complexes show that the electrochemical processes in the anodic region are controlled both by kinetic and diffusion factors, whereas the primary influences in the cathodic region are associated to kinetic factors arising from the alkyl chains [68].

6.5. Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) constitutes a technique of fundamental importance for the characterisation of NPs and NP-polymers, in particular of NP-PTh composites. In principle, it is possible to measure directly the shape, diameter and size distribution of the NPs. The results reported in the literature as to the metal core mean size for the NP-PTh composites vary over a wide range, reflecting the large number of different preparation methods and the strong influence, on the characteristics of the final material, of slight variations in the experimental parameters, even when the composites are prepared using the same general procedure.

Useful information concerning the degree of eventual aggregation/coalescence of NP cores can be obtained by TEM measurements. This phenomenon has been often observed in the case of soluble NPs deposited on a planar surface [249,264]. The aggregates can possess an ordered structure: in particular, 2D aggregates arising on a planar surface can assume an hexagonal symmetry, as reported in the case of Au NPs encapsulated by poly-(3-hexylthiophene) [249]. The formation of these regular structures is strongly dependent on *i*) the nature of the NPs and, in particular, the nature of the encapsulating agent; *ii*) the size distribution of the cores, a narrow size distribution being mandatory for the formation of large, well ordered aggregates.

The mean atomic numbers of the atoms constituting metal, as well as metal oxide NPs, is usually very different from those of the atoms of the PTh matrix, so that, in principle, the cores of the NPs can be easily distinguished from the organic matrix. Hence, the actual formation of a NP-PTh composite can be verified. Moreover, although in most cases the preparation procedures are designed in order to obtain NPs homogeneously dispersed inside the polymeric matrix, the possible (partial) segregation of the components can be checked.

The electron transmittance of the sample as a whole may present a major limitation: when the thickness exceeds approximately 100 nm or when the composites contain a large fraction of metal NPs, the transmittance drops dramatically. As a result, the sample preparation constitutes a critical step for a successful characterization. When the composite is soluble, a drop of the solution can be deposited onto a suitable grid coated by a suitable support material, such as Formvar[®], that forms a very thin and electron-transparent film on the grid. Then, the solvent is removed by evaporation and a very thin, electron transparent layer of composite remains on the coating of the TEM grid. This kind of samples can be characterized by TEM without any further preparation steps [249,254,258,260,261,264,276,279-281,283].

A similar approach has been also adopted for the study of NP aggregates dispersed in solution [210]; in particular, it was possible to verify that the distance among the NPs in aggregates is related to the size and orientation of the Th molecules adsorbed on NP surface. Although this method is widely employed due to its simplicity, some artifacts can be introduced; as an example, the de-wetting process can alter the structure of the composites and the degree of aggregation of the NPs [260,276].

In most cases the PTh composites are highly insoluble, so that it is not possible to directly deposit a solution of the composite onto the TEM grid. However, synthetic methods for PTh-NP composites lead to the formation of a fine powder that can be suspended in a suitable solvent and deposited onto a coated grid [238,284,335]. This preparation procedure is rather popular in the case of metal oxides coated by a thin layer of PTh [308,320]. Alternatively,

insoluble film floating on a liquid surface can be skimmed off by means of the TEM grid itself [266].

In many practical applications, the PTh-NP composites are under the form of films. As a result, special preparation techniques must be adopted. A reported method consists in depositing fragments of the polymer coating, peeled out from the underlying support material, on a suitably coated grid [269,271,272,274]. Alternatively, very thin films can be grown directly on either coated or uncoated TEM grids [229,275]. In the case of coated grids, the choice of the coating material is rather limited (Formvar[®], Formvar[®]/C, SiO₂), while the uncoated grids are normally made of metals, such as Cu, Au or Ni. In any cases, it is difficult to determine the exact localization of the NPs inside the film. In particular, it is difficult to verify whether proper NPs or NP aggregates constitute charge percolation pathways through the film. With this respect, electrochemical and conductivity measurements can be more useful.

The contamination, i.e. deposition of carbonaceous species induced by the electron beam on the region of the sample under investigation, as well as damages induced by the electron beam itself, are rather common in the presence of organic matter. Hence, cooling the microscope chamber walls and the sample is often of definite help.

As to the shape, large NPs are rather similar to bulk crystals; in this case, SEM measurements have been also employed for the characterization (see Section 6.6). On the contrary, the shape of small NPs, i.e. below few tens of nm, is rather different; in particular, as already discussed, NPs possess a polyhedral shape that can be only roughly approximated to a sphere. Actually, it is difficult to ascribe definite shape to a single small NP, since *i*) the mobility of the atoms on the surface of metal NPs is significantly high even at low temperature; *ii*) different shapes are energetically very similar to one another at room temperature, so that transitions between different shapes is often reported, also due to the additional energy supplied to the NPs by the TEM electron beam; *iii*) NPs are generally highly defective, due to the release of internal stresses, and each NP is often composed by more than one crystal domain.

High resolution images, i.e. images which even evidence the single atoms, are only rarely reported [336], since the presence of the organic matrix induces contamination phenomena and high degree of mobility of the NPs inside the polymeric matrix is well possible. However, the presence of a thin layer of PTh on the surface of large metal oxide particles, or intercalated between the layers of oxide nanostructures, allows high resolution to be reached [308,318].

The nature of the polymeric matrix is basically amorphous and no fine details or nanostructures can be detected by TEM. However, some authors prepared composites in which the synthesis of the polymeric matrix or of the composites is addressed by a suitable template. Different nanostructures based on PTh were observed in these cases, such as nanocones [246], nanotubes [274] and fibrils (see Section 6.6). Finally, in the case of oxides intercalated with PTh, the presence of PTh between the oxide layers has been verified [318].

Obviously, TEM has been also employed for the characterization of the NPs synthesized before the formation of PTh-NP composites [210,264,267,268,287,295,296].

6.6. Scanning Electron Microscopy, Atomic Force Microscopy and Scanning Tunneling Microscopy

The morphology of PTh films embedding metal ions and NPs, deposited on a support material, has been investigated mainly using Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM). Literature reports different possible morphologies of CP coatings, depending on the nature of the polymer, of the underlying support material, of the solvent medium used for growth, and of the methodology used in the deposition, i.e. casting, spin coating, or electrodeposition by potentiostatic, galvanostatic, or potentiodynamic techniques [337]. The addition of a second component, especially in the case of NP inclusions, further complicates the dependence of the morphology on the film formation experimental parameters.

Most authors have observed the formation of relatively corrugated surfaces [239,248,208]; moreover, the presence of NPs inside the polymeric matrix may strongly alter the morphology of the film with respect to that of the pristine polymer [208,271,272,323]. When the composite film is prepared using electrochemical techniques, a granular texture has been often observed on the coating surface [271,272]. The polymerisation process involves the formation of oligomer chains in solution and the subsequent precipitation of polymer onto the electrode surface, once the solubility limit is exceeded. The size and size distribution of the grains are dependent on the experimental parameters used in the deposition. However, the NPs do not seem to constitute the nucleation seed for the polymer grains, since many NPs are distributed inside each one of them. Some authors have reported the formation of a relatively smooth surface possessing minor bumps and depressions [326]. Only in few cases nanostructures such as fibrils have been observed by SEM [215,216] or AFM [249].

In the case of SEM, the sample preparation is often simple: no metal coating on the surface of the samples is generally necessary in order to impart electrical conductivity to the system under investigation, thanks to the intrinsic conductivity of the PTh matrix. In most cases, the thickness of the film is relatively high (few hundreds of nm); hence, the influence of the roughness of the underlying support material is negligible. Some authors also report the possibility to prepare and characterise cross sections of the polymeric film in order to investigate the arrangement of the NPs inside and to estimate the film thickness [266].

The majority of the SEM instruments are capable to generate images of large NPs located at the composite surface [215,219,234,240]; in some cases the polyhedral shape of the crystal has been evidenced [240]. Only some authors report also high resolution images of relatively small NPs, typically below 50 nm [262,277]. The formation of NPs on the surface of a conducting polymer film by electrodeposition constitutes an interesting situation. The size, size distribution and the distribution of the metal cores on the surface bring important information on the mechanisms controlling the formation of the NPs. Experimental characterizations are often coupled to theoretical simulations of the nucleation process [137,151]. If the NPs are small (below 10 nm) and dispersed inside the polymeric matrix, TEM is normally preferred for the characterization, since no useful information can be generally drawn out from the knowledge of the morphology of composite films, especially when the thickness is relatively high. In the case of metal oxide NPs, SEM has been used in order to verify the occurrence of the polymerization on the surface of the oxide nanostructures or inside the oxide framework, as in case of layered oxides [308].

Also analyses performed using SEM present some drawbacks. Similarly to the case of TEM, the electron beam can induce damages in the sample surface. Moreover, SEM is normally performed in vacuum, although in recent years Environmental SEM (ESEM) instrumentation has been developed, allowing the analysis at relatively high pressure, though not exceeding few tens of torr, which is a limit quite far from the ambient pressure.

In the case of AFM, the sample can be characterized without any additional preparation steps. Samples can be characterized employing many different methodologies, such as contact [267,288], non-contact [278,210], tapping [249,262,297], phase imaging [249,254] and friction force imaging [288] modes, normally performed in air.

In principle, AFM can achieve atomic resolution. In the case of PTh-NP composites, such a high resolution is however difficult to achieve, since the polymeric matrix is basically amorphous and the NPs are generally very small and surrounded by the polymeric chains. The possibility to identify single NPs on the polymer surface is also complicated by the tip-sample convolution, which generates artefacts, such as the 'virtual' increase of the lateral size of the objects present on the surface. Additional difficulties arise from the presence of the polymer matrix possessing granular morphology similar to that of the NPs, as in the case of some electropolymerised composites; furthermore, it is difficult to distinguish regions possessing different chemical composition. Some attempts to determine the mean size of the NPs have been performed depositing an ultrathin film of soluble PTh-NP composites on atomically flat surfaces, such as freshly cleaved mica [270] and highly oriented pyrolytic graphite [258]. Under suitable conditions, this methodology leads to the formation of a monolayer of NPs on the surface; the NPs may be individually isolated [270] or form 2D aggregates [258]. However, it is obvious that such an approach requires at least an additional independent estimate of the NP size, for example using TEM.

SEM [234], AFM [262,264] and stylus profilometers [208,210,278] were used for the determination of the thickness of the composite films. In many cases the thickness is calculated on the basis of the height of the layer of composite with respect to the underlying substrate in the correspondence to the border of the film. Alternatively, the thickness has been calculated from the profile of a scratch made on purpose. PTh-NP composites are reported to form films possessing a thickness ranging from few nm to few μm , depending on the experimental procedure and on the parameters used for the film deposition. Most measures were obtained on dry films in air; it is however worth noticing that the thickness can be significantly different when the composites are in contact with solutions, even not considering that significant swelling and shrinking of the polymeric matrix are induced by cycling the potential between charging and discharging values.

Recently, alternative effective methods for the determination of the film thickness of PTh in liquid phase have been developed, such as ellipsometry [229]. These methods have not been used extensively for the characterization of PTh-NP composites so far, although some attempts have been carried out.

STM is rarely used in the case of PTh-NP composites, probably because the experimental problems concerning the instrumentation, in particular the tip, are more difficult to solve with respect to AFM. However, some attempts have been made on electrogenerated poly(3-octylthiophene) including 2-mercapto-3-octylthiophene capped Au NPs [270] and on dodecanethiol capped Au NPs deposited by Langmuir-Blodgett technique together with compound 47 [297]. In addition, STM apparatus have been used for Scanning Tunnelling

Spectroscopy (STS) in order to determine the current-potential characteristics, in particular to verify the occurrence of the so-called ‘Coulomb blockade phenomenon’ [297].

6.7. Energy Dispersive Spectroscopy

Energy Dispersive Spectroscopy (EDS), suitable for a qualitative and semi-quantitative analysis of the atoms in the close proximity of the film surface, is often coupled to TEM and SEM. The electron beam can be focused on a particular spot of the sample, even allowing the analysis of the composition of a small portion of the PTh embedding metal ions or NPs. Characteristic X-rays are generated by a volume of matter that depends on the experimental conditions; generally, this volume is relatively large in the case of SEM (at least hundreds of nm³) while in the case of TEM the volume can be reduced down to few nm³, allowing the characterisation of even a single isolated NP. Obviously, the signal-to-noise ratio often decreases when the volume is too small.

EDS is not suitable to achieve an exact evaluation of the metal loading inside the polymer matrix: the limit of detection is relatively high (roughly 1% w/w), suitable standards are often unavailable and, in the case of thin films, the characteristic X-rays originating from the underlying substrate often overlap the signal sought and may dominate the spectra. However, the occurrence of the deposition of the polymeric matrix [281], the qualitative analysis of the metal inside the composite [170,227,248,267,269,279,336] and relevant semi-quantitative analyses [208,219,224,239,240,250,252,338] have been performed, sometimes confirmed by independent measurements, e.g. by XPS. Moreover, EDS can not distinguish the different oxidation states of the metals, i.e. it is not possible to discriminate between metal atoms and relevant compounds, such as metal salts, complexes, or even oxides. However, some information concerning the chemical reactions occurring during the formation of the composites can be drawn from EDS spectra. As an example, anionic complexes of the metal of interest are normally employed in the synthesis of the composites. The reduction of these anions leads to the formation of zero-valence metals and the anions are normally washed out. The lack of signals relative to the ligand of these complex anions, together with the presence of the signals of the metal in the spectra of the composites, constitute a proof of the occurrence of the reduction reaction [239]. Moreover, the presence of metal and of oxygen suggests the formation of a significant fraction of metal oxide instead of pure zero-valence metal NPs [282].

XPS (see Section 6.9) constitutes a complementary technique suitable for gaining information on the oxidation state of the elements in the composites. Finally, EDS coupled with SEM and TEM has been used for the investigation of possible macroscopic and microscopic segregation of the components constituting the PTh-Au NP composites, i.e. the formation of large aggregates of NPs inside the composite [272].

6.8. Rutherford Backscattering Spectrometry

Rutherford Backscattering Spectrometry (RBS) [339] has been employed only in few cases as a complementary technique for the determination of the composition of thin films based on PTh-NP composites [223,239] and on PTh-based metallopolymers [50]. Despite the

potential high sensitivity and high depth resolution of this technique, combined with the possibility to perform the analysis without destroying the sample, the complex and expensive experimental setup prevents from wide diffusion of this technique.

6.9. X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) has been often employed in the study of polymers, in particular of PThs [240]. XPS has been used to study the chemical composition and the oxidation state of the atoms in hybrids and composites, taking advantage of the sensitivity of the chemical shift of the relevant peaks. In some cases, quantification of the different chemical species has been performed. This is particularly important in the case of metallopolymers, both in order to verify the integrity of the complex after the electropolymerisation process [45,62,64,91] and to define the extent of complexation when it is carried out after the electrogeneration of the organic polymer containing suitable ligands [45]. Moreover, it is also possible to define the actual oxidation state assumed by different atoms in the film, as a consequence of oxidation or reduction of the coating [62,64,91,94,170], also in order to check the actual reduction of the metal salts to zero-valence metal [209,215,229,248,255,270,281,310]. The chemical shifts of the C1s and S2p peaks have been fruitfully used to acquire information on the possible oxidation of the polymeric backbone [317]. Moreover, the occurrence of the oxidation of the polymeric matrix has been verified on the basis of the presence of foreign atoms ascribed to dopants, such as iron complexes [317]. As to metal oxide NPs, some authors reported the occurrence of charge transfer between the NPs and the polymeric matrix, evidenced by a significant shift of the photoemission signals ascribed to the metal [313,320]. In the case of metal NPs, most authors deduce from XPS measurements that the metal salts are quantitatively reduced to zero-valence metal. However, it is worth noticing that the limit of detection is not particularly low (ca. 1-5%): small concentration of such species as oxides or anions, located at the NP surface, deeply influences the reactivity of the NP, though being not detectable by XPS. Moreover, XPS can only probe the outermost region of the sample, so that only the NPs located at the surface of the polymer coating are detected; in addition, when the NPs possess a large diameter, only the signal ascribed to the outermost regions of the NPs is detected. In principle, it could be possible to characterize the bulk of the polymeric matrix by coupling XPS with Ar⁺ ion sputtering [341].

The sample preparation for XPS measurements is quite similar to that reported for SEM. It is worth noticing that XPS requires ultra high vacuum conditions, otherwise suffering from the drawbacks previously discussed for TEM and SEM; in addition, eventual alterations of the composites induced by X-rays should be carefully taken into account.

6.10. X-ray Absorption

Techniques based on the absorption of X-rays [342], in particular Near Edge X-ray Absorption Spectroscopy (NEXAFS) and Extended X-ray Absorption Spectroscopy (EXAFS) have been used extensively for the study of Th monomers, oligothiophenes and pristine PTh, both under the form of bulk samples and of thin films anchored to substrates.

On the contrary, these techniques have been only occasionally used in the study of hybrids [62,85,90,172] and of PTh-NP composites [214,216,218,222,234,235]. In all cases, NEXAFS gives information concerning the oxidation state of the different metal species and EXAFS on the coordination sphere of the metal ions and atoms. In the case of PTh-NP composites, these spectroscopic techniques were also exploited in order to study the mechanism of electrodeposition of Pt, Cu, Pd and Fe NPs on P3MT and PTh films. In these cases, the experiments were performed *in situ*, by using an *ad hoc* developed cell. The growth of the NPs was studied employing both dispersive NEXAFS and EXAFS, which also gives a measure of the mean size of the NPs. The most part of these experiments was carried out in time-resolved mode; this aspect is particularly important since the growth of the NPs is a relatively fast process and, therefore, difficult to investigate. The main drawback of such a kind of studies consists in the necessity of using synchrotron radiation facilities, the access to which, and even proper management of the measurement procedures, are often not so easy. Moreover, the fitting procedure of the EXAFS spectra is not straightforward, and suitable literature should be consulted.

6.11. Diffraction Techniques

Electron diffraction, carried out using TEM instrumentation, has been widely employed in the case of bulk samples, but only occasionally used in the case of PTh-NP [280,281,336], since the samples are formed by a large number of separated metal cores, being hence of polycrystalline character. The resulting diffraction pattern is not constituted by well defined spots, but only by concentric rings, the reciprocal distance being related to the lattice spacings.

X-ray Diffraction (XRD) has been used for the identification of the crystal structure of the NPs in PTh-NP composites, when they are under the form of powder or of thin film. If the fraction of metal inside the polymer is high enough, the diffraction patterns exhibit the typical sharp peaks corresponding to metal lattice planes [238,276,280,281]. Moreover, in the case of oxides intercalated with PThs, the distance between different layers has been investigated, such as in the case of V_2O_5 [308,310]. XRD can be also used for a qualitative compositional analysis of the NPs, since the peak positions and intensities depend on the actual crystalline phase, i.e. on the chemical nature of the NPs. The size of the NPs can be determined employing the well known Debye-Scherrer equation, which correlates the broadening of the peak with the mean size of the crystallites [210,219]. Furthermore, small angle diffraction has been used for the determination of the spatial distance between the metal cores [276]. Unfortunately, the diffraction patterns can suffer from some limits, such as the impossibility to detect the presence of amorphous phases, the possible formation of metal compounds on the NP surface, and the dependence of the lattice cell parameters on the synthesis conditions [343].

XRD has been also used for the determination of the spatial arrangements of the chains in PTh derivatives. Highly ordered structures have been reported for pristine polymers [344] while, in the case of composites, the crystal structure of the polymeric matrix has been poorly investigated, although the results suggest that its nature is basically amorphous [338]. The sample preparation is similar to that reported for SEM and AFM in the case of thin films, but also powders are routinely characterised.

6.12. Inductively Coupled Plasma Spectroscopy

The metal loading of the PTh-NP composites has been quantified by gravimetric analysis and by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) [246,271,272]. As to the sample preparation, the PEDOT matrix has been successfully mineralised in alkaline solution and Au NPs similarly mineralised by oxidation with *aqua regia* [217,272]. Alternatively, the metal fraction has been 'extracted' from the polymeric matrix by means of strongly oxidizing solution, such as, once more, *aqua regia* [246].

6.13. Thermal Analysis

The metal loading of PTh-NP composites can be also determined using Thermo Gravimetric Analysis (TGA) and combustion of the composite in muffle. The destruction of the polymeric matrix is performed by heating the composite in air at high temperature (300-600 °C). The exact decomposition temperature depends on the preparation method of the composites [252,269,274]. In particular, the decomposition temperature depends on the degree of oxidation of the polymeric matrix when the dopant anions contain heavy metals [317], the oxidized form of PTh being decomposed at lower temperature than the neutral form. This dependence has been exploited for the determination of the fraction of PTh in the neutral state. A decrease of the decomposition temperature has been also observed in the case of composites containing metal oxide NPs [320]. Heavy metal complexes, dopants and metal oxide NPs are considered effective catalysts for the thermal decomposition processes. In some cases [336] it was verified that the low temperature thermal treatment has to be followed by a suitable chemical treatment in order to complete the demolition. It is evident that other phenomena take place during the thermal treatment, such as water release, oxygen uptake [307] to form metal oxide NPs, and metal oxide phase transition [310]; with this respect, TGA has been coupled to Differential Thermal Analysis (DTA) in order to identify endothermic and exothermic processes [307]. Some authors reported the possibility to thermally remove the organic matrix of a PTh-NP composite grown inside the pore of a suitable template, in order to obtain pure metal nanowires [274]. In addition, when a monolayer of Th-based molecules is chemisorbed on the surface of metal NPs, TGA has been also used in order to calculate the packing density of these molecules [276] and to possibly confirm the elemental analysis data obtained by XPS [208]. The quantification is carried out assuming that only metal species are present at the end of the thermal treatment. Finally, the thermal stability has been estimated using TGA [284]: PTh-Ag NP composites seem to be more stable than the corresponding pristine polymeric material.

6.14. Vibrational Spectroscopies

IR and Raman spectroscopies are very diffusely used in the studies of materials based on PThs [345-347]. In the case of PTh hybrids and composites, IR spectroscopy has been applied to dry powders, both pure [276,280,284,338] and dispersed inside KBr pellets [47,208,211,229,258]. Alternatively, IR spectra of thin layers of composite solutions have been acquired by depositing few drops of liquid between IR-transparent windows [281]. In

addition, IR spectra have been also collected on PTh hybrids and composites, mainly obtained by electrogeneration, under the form of dry thin film deposited on a substrate [45,107,109,210,229].

IR spectroscopy has been successfully used also coupled with electrochemical techniques, i.e. in a suitable spectroelectrochemical cell [348]. This approach, when applied to the investigation of PTh-based metallopolymers [62,76,79,114], gives important information regarding the charge and discharge processes of the film. In the case of PTh-NP composites, the use of similar *in-situ* studies has not been reported yet.

IR technique has been employed in order to confirm the actual oxidation of the monomer to the relevant polymer [47,107,109,276]. The C-H stretching vibrations involving C atoms located in α position with respect to S atoms in Th rings are diagnostic with this respect. The reduction of the signal intensity of these vibrations has been monitored in order to confirm the occurrence of the α - α' coupling reaction between Th rings due to chain growth, and contemporary Au(III) reduction [280,281,338].

Acetyl groups are routinely employed for the protection of -SH groups [210]; the formation of a free -SH group is ascertained by the disappearance of the C=O vibration. Finally, other diagnostic vibrations have been exploited to confirm the presence of PTh in the composites [279].

IR spectroscopy has been also used to verify the presence of some by-products of the composite formation. As an example, in ref. 208 phosphine oxide is detected as an oxidation product of phosphine ligand present in the starting metal complex used in the NP synthesis. In addition, the interactions inside the hybrids and composites can strongly modify the IR spectra of the polymeric matrix: in particular, it was possible to verify: *i*) the importance of hydrogen bonds inside a multilayer grown by LbL technique [229]; *ii*) the presence of interactions of the polymeric matrix with metal ions such as Ag(I), Pd(II), and Au(III) [284,259] or with Pd NPs [259] dispersed inside a composite; *iii*) the occurrence of complexation reaction between a polymer film containing bipyridine metal ligands and Re(I) in solution [45].

When a monomolecular layer of Th derivative is anchored to the NP surface, IR spectroscopy has been employed in order to acquire information about the degree of order of the monolayer [258]. The presence of characteristic vibrations ascribed to metal oxide NPs [320] or POMs [299] has also been reported, even allowing hypotheses to be advanced with respect to the oxidation states of the metal [307]. Finally, exposure to NO₂ gases of a film based on different PThs containing SnO₂ leads to significant reversible modifications of the IR spectrum, ascribable to the occurrence of oxidation by NO₂ [325].

It is worth noticing that the signals in IR spectra can be strongly enhanced when the absorbing species are adsorbed on rough surfaces, such as those of small metal NPs. This phenomenon has led to the development of Surface Enhanced InfraRed Absorption (SEIRA) technique [349]. This technique has allowed the determination of the molecular orientation of terthiophene on Au NPs with respect to the surface, thanks to the surface selection rules [211]. The interpretation of the spectra has been also supported by Density Functional Theory (DFT) calculations [211].

Raman spectroscopy constitutes a complementary technique to IR spectroscopy. Analyses have been normally carried out on composites consisting of dry powders [276,280,318] or dry thin films [236,271,272]. The coupling of Raman spectroscopy with

electrochemical techniques has not been explored so far. Raman spectroscopy has been carried out in order to confirm the formation of a polymeric matrix surrounding the NPs, by oxidation of the monomer [276]. Raman instrumentation can be profitably coupled with an optical microscope in order to acquire spectra in localised region. Using such an experimental setup, some authors demonstrated the formation of the polymeric matrix around metal nanotubes [236]. In addition, Raman spectroscopy can be employed in order to estimate the doping level of the PTh matrix; however, in the case of the PTh-NP composites, this possibility has been rarely used so far [280,318]. Some authors report that the absence of differences between the Raman spectra of pristine PTh and those of the corresponding PTh-NP composites suggests that the presence of metal does not affect the overall nature of the polymer [271,272,338].

In all cases, it is worth underlying that possible damages induced by Raman lasers should be taken into account, since they can severely alter the spectrum recorded [350].

PTh-NP composites have been prepared through encapsulation of NPs by different Th derivatives in order to study the vibrational spectra of similar encapsulating agents. It is well known that the Raman signals can be strongly enhanced when molecules are adsorbed, for example on the surface of metal NPs. The most effective metals with this respect are Ag and Au. This technique is called Surface Enhancement Raman Spectroscopy (SERS) [350]. It is evident that similar studies are of key importance when the results are extended to the composite materials described in Section 3 and 4; in particular, these investigations contribute to elucidate the nature of the interface between the polymeric matrix and the metal NPs, also allowing the determination of the molecular orientation with respect to the surface, thanks to the surface selection rules. The majority of the studies are focused on simple Th derivatives; in these cases the adsorption on the NP surface is normally carried out by adding the molecules under investigation to a dilute NP solution (see, e.g., ref. 351). As to PThs, the studies are limited by the poor solubility of the polymers. However, oligothiophenes [352,353] and poly(3-alkylthiophenes) [354,355] have been studied once adsorbed on the surface of Ag NPs, synthesised in advance - for the NP synthesis see, e.g., ref. 356. The possible polymerisation of Th derivatives on a non-totally reduced Ag surface has been also reported [357]. In addition, PTh films, such as P3MT, poly(3-butylthiophene) and poly(3-octylthiophene), can be coated by a discontinuous layer of electrodeposited Ag NPs, leading to strong enhancement of the signal due to the portion of the composite film in close contact with the particles [351]; alternatively, Ag NPs can be electrogenerated inside the polymeric matrix (see Section 4.1.1) [355].

Additional nanostructures have been prepared with the specific purpose of enhancing Raman signals. As an example, dendritic Au nanostructures have been synthesised at the interface between an aqueous solution containing HAuCl_4 and a dilute solution of EDOT in dichloromethane [336]. A redox reaction leads to the formation of PEDOT and of Au dendrimers; PEDOT has been successively removed, leading to the obtainment of Au nanostructures with high surface/volume ratio.

6.15. Electron Paramagnetic Resonance

Despite the abundant literature dealing with CPs and even PThs, very scarce attention has been devoted to the characterisation of hybrids and relevant composites by Electron

Paramagnetic Resonance (EPR) technique [60,79,87,241]. When analysing PTh-based materials, the EPR sample can either consist of a powder or of a thin film coating the working electrode in a suitably designed electrochemical cell. PTh-NP composites are generally investigated under the form of fine powder. In the case of metal oxide NPs, useful information have been drawn out from EPR studies, concerning the stoichiometry of the oxide species; as an example, the presence of V^{4+} species in V_2O_4 has been verified [308]. On the contrary, PTh-based metallopolymers are generally investigated through *in-situ* EPR measurements, i.e. in a suitable electrochemical cell, in order to study the charge carriers inside the film, at different applied potentials [60,79,87].

6.16. Other Optical Characterizations

Dynamic Light Scattering (DLS) constitutes one of the most important techniques in the field of colloid science. In the frame of PTh-NP composites, this technique is complementary to TEM, since TEM basically measures the size of the metal core, while DLS is suitable to measure the hydrodynamic diameter of the NP, encapsulating shell included [280]. Unfortunately, in the case of a composite, a solution/colloidal suspension is only rarely obtained, preventing the characterization of most composites prepared so far. Moreover, if the sample is composed by a mixture of particles possessing different diameter, the results from DLS are sometimes unreliable.

As to photoluminescence, the NP metal cores are well known quenchers of the photoluminescence of many chromophores, including some Th derivatives [258]. The quenching yield is a function of the distance of the Th-based chromophores from the metal core surface; however, different effects have been also reported. In the case of a composite of Au NPs, encapsulated by long thiol molecules, with PTh, under the form of thin film, an increase of the photoluminescence yield has been observed [262]; this increase seems to be related to morphological and/or structural factors, since the presence of Au NPs modifies the arrangement of the polymeric chains. However, the photoluminescence properties of these films seem to be spatially inhomogeneous [260,261]. Moreover, the insertion of Au 'nanoshells' inside the polymeric matrix seems to alter the de-excitation mechanisms, leading to a decrease of the photo-oxidative degradation [263]. Further studies are necessary in order to clearly understand the effects of the NPs on photoluminescence phenomena.

Probe Beam Deflection (PBD) technique has been used for the investigation of the region of solution close to a surface, namely the working electrode in an electrochemical cell [358]. In particular, it is possible to follow the formation of films on the electrode surface and the release of species from the electrode coating, since the refraction index of the solution is strongly influenced by mass fluxes. The simplicity of the apparatus favour the use of PBD in time-resolved experiments coupled with potentiodynamic techniques. In the case of PTh-NP composites, PBD was used in order to indirectly elucidate which metal deposition method leads to the highest metal loading [227].

Laser diffraction is a routine technique for the determination of the size of relatively large particles. However, this technique has been only occasionally applied to the study of PTh-NP composites [245].

Finally, it is worth noticing that the irradiation of PTh coatings with light sources possessing a high intensity in the UV-Vis range induces the occurrence of measurable

photocurrents and even of de-doping processes. These phenomena have been studied in developing *photovoltaic devices* [359,360]. However, only few experiments have involved the use of PTh-NP composites [225] and PTh-based metallopolymers [52].

7. SELECTED APPLICATIONS

In spite of the large number of papers concerning the development of hybrid and composite materials based on PTh, only a minor fraction deals with possible applications. In the present section, only selected applications, chosen among those that exploit the electrochemical properties of these materials, are exposed.

7.1. Amperometric Sensors

The development of amperometric sensors based on hybrid and composite materials constitutes a fast growing field of research. Recently, similar electrode systems, for detecting specific analytes such as ascorbic acid [164,169,268,271,273,326], dopamine [164,169,268,271,273,326,362], uric acid [268,273,326,362], glucose [224], 2,4,5-trichlorophenol [105], NO₃⁻ ions [243], have been proposed, although often at quite a preliminary stage of development. Moreover, the real advantages with respect to electrodes modified with the pure organic material are not always discussed.

A metallopolymer based on Fe-porphyrin complexes has been used for the determination of 2,4,5-trichlorophenol at a concentration as low as 0.8 mM [105]. The presence of the phenol derivative induces a significant shift of the metal-porphyrin redox system to more negative potential, as evidenced by the CV responses. The shift is claimed to be proportional to the analyte concentration and is ascribed to interactions and complexation of the Cl atoms with Fe centres that, in turn, induce changes in the electronic structure of the porphyrin ligand.

As to dopamine, it is well known that its determination in biological samples is particularly important; however, the presence of interfering species, such as ascorbic and uric acids, renders the determination challenging. Different modified electrodes have been proposed in order to overcome this problem; the use of PTh-based hybrid and composite materials represents one of the recently outlined possibilities. Differential pulse voltammetry is normally employed in this case as the electroanalytical technique, in order to improve the resolution of the single responses, to increase the sensitivity of the electrochemical responses, and to lower the detection limit [361]. Definite advantages with respect to the pure organic material were observed in the case of several PTh-NP composites. In these cases, PEDOT electrode coatings have been electrogenerated either in the presence of different kinds of NPs dissolved in solution together with the monomer [272,273], or by directly polymerizing EDOT encapsulating metal NPs [268,273,326]. In the case of the composite containing Au NPs encapsulated by EDOT [268,273,326], the presence of the inorganic component has been reported to significantly improve the selectivity, sensitivity and detection limit, with respect to the pristine polymeric matrix; the calibration plot resulted linear in the 2-20 nM range for dopamine and uric acid. In this case, the improved performances of the device are ascribed to

a different selectivity of the analytes for different ‘hydrophobic’ and ‘hydrophilic’ regions of the film, also induced by the presence of NPs.

A different approach takes advantage of electrostatic interactions, exploiting the fact that in neutral phosphate buffer solution ascorbic acid and dopamine are negatively and positively charged, respectively. The signals ascribed to their electrooxidation have been tuned by varying the loading, inside the polymeric matrix, of Au NPs surrounded by negatively charged encapsulating agents, namely species 36 or 37 [271,272]. In both cases, a significant lowering of the ascorbic acid signal has been observed, due to electrostatic repulsion with the negatively charged cloud of the NPs. Concurrently, a significant increase of the sensitivity in detecting the positively charged dopamine has been also observed when using tannic acid as the encapsulating agent.

Pd NPs electrodeposited on PEDOT have been employed for the simultaneous determination of dopamine and uric acid in the presence of a large excess of ascorbic acid. In this case, the composite material exhibits a higher sensitivity with respect to the single constituents; the calibration plot is linear in the 0.5-1.0 μM and 7-11 μM ranges for dopamine and uric acid, respectively [362].

PEDOT electrode coatings embedding Cu(II) ions and Cu, Pd and Cu-Pd NPs have been employed in the electroreduction of NO_3^- ions in neutral solution. These systems have been prepared through electrodeposition and galvanic exchange reactions [243]. Cu NPs show the capability to promote NO_3^- ions electroreduction; on the contrary, Cu(II) ions trapped inside the polymeric matrix have demonstrated to be effective in hindering hydrogen evolution, but ineffective in promoting NO_3^- reduction. This is a very important aspect, since hydrogen evolution interferes with the determination of NO_3^- ions. On the contrary, Pd NPs promote hydrogen evolution and, therefore, possess a detrimental effect on NO_3^- reduction. Interestingly, bimetallic Cu-Pd systems seem to be most effective: the synergic effect of the two metals induces NO_3^- electroreduction and effective prevention of interfering hydrogen evolution.

Cu_2O and CuCl particles have been electrodeposited on electrogenerated P3MT coatings [224]. These modified electrodes have been employed for the determination of glucose in basic medium, but only preliminary results have been reported so far.

Very recently, an innovative application of composite modified electrodes in the field of sensing has been proposed; similar electrodes have been tested as elements of so-called *electronic tongues*. In this case, electrodes modified both with pure PEDOT and with PEDOT-Au NP composites show good classification ability of different white wines [363].

7.2. Potentiometric Sensors

Very few examples of the use of hybrid or composite materials in potentiometric sensors have been reported so far. The efforts have been focused on the development of all-solid-state ion-selective electrodes, consisting of an electrode substrate coated by hybrid materials. As an example, PEDOT doped with FeCN ions has been employed for the determination of Cu(II) ions [165]. The resulting electrode system exhibits a good selectivity towards interfering species such as Ni(II), and a detection limit as low as 10^{-7} M. Alternatively, an ion-selective polymeric membrane has been also deposited on the just described hybrid material thin film.

As regards the metallopolymers, a modified electrode obtained through electropolymerisation of the uranyl salen complex 2 has been employed for the determination

of monohydrogen phosphate [58]. The detection limit is quite low (10^{-5} M) and the response time is fast (<10 s).

7.3. Conductivity Sensors

Sensors based on conductivity variations of PTh-based hybrids or composites have been developed for the determination of analytes in liquid and gas phase.

Hybrid materials based on Co-salen complexes directly inserted in the polymer chain, deriving from electropolymerisation of compounds similar to 3, have been employed for the determination of NO [63,64]. The hybrid material, deposited on interdigitated electrodes, has been exposed to NO concentrations as low as 1 ppm, at 40°C, showing a marked and reversible decrease of conductivity at increasing the NO concentration. Interestingly, the pristine PEDOT polymer does not show any significant conductivity variations. The conductivity change observed in the case of the hybrid material has been ascribed to the transition of the Co metal centre from four- to five-coordination, to include NO in the apical position. The possible interference of species such as O₂, CO, CO₂ and NO₂ has been tested: only the exposure to NO₂ induces irreversible increase of the conductivity.

The detection of pyridine, 2,6-dimethylpyridine and 2,6-di-tert-butylpyridine in acetonitrile solution has been carried out on a Co-salen modified electrode very similar to that just describes [57,59]. In this case, the reversibility of the conductivity variation constitutes a critical point, particularly in the case of pyridine and 2,6-dimethylpyridine.

Co-phthalocyanine/poly(3-octadecylthiophene) thin films, deposited through LB technique, have been employed for detection of NO₂ and NH₃ at room temperature [369]. The performance of the electrode system, in terms of reversibility and response time, depends on a number of variables, such as the composition of the hybrid material and the thickness of the film.

Poly(3-hexylthiophene) and PEDOT including SnO₂ and TiO₂ have been employed for the detection of NO₂ and CO [325]. The electrode system consisted of four-band or interdigitated Au electrodes. The exposure to NO₂ or CO, even at ppb level, leads to a marked increase of conductivity. This change is ascribed to the formation of a p-n junction between the metal oxide and the polymeric hosting matrix, the energy band structure of the junction being strongly affected by the exposure to the gases. The response of the sensor is very fast, at variance with what observed in the case of the system of the two oxides.

P3MT thin films electrogenerated on interdigitated Pt electrode have been modified by electrodeposition of Cu inclusions [226]. A significant increase of the resistance has been observed when the electrode system was exposed to hundreds ppm of reducing gases, such as NH₃, at 50°C and 100°C. Unfortunately, details concerning the influence of the inclusions on the behaviour of the sensor, with respect to pure P3MT, are missing.

7.4. Fuel Cells

In the field of fuel cells, electrocatalysis plays a key role [364]. Hybrid materials based on metal complexes and PTh derivatives have been rarely used in this frame, being only limited to fundamental studies. As an example, Co- and Cu-phthalocyanines have been employed for the electroreduction of H₂O₂ in basic medium; the complexes have been

deposited on a P3MT thin film [180]. In addition, the previously reported Co-salen metallopolymer has been employed for the catalytic electroreduction of O₂ in phosphate buffer solution [61]; in this case, the nearly complete conversion of O₂ to H₂O is mainly ascribed to the highly conductive nature of the polymer film, which allows a fast electron transfer from the electrode to the catalytically active metal centres. Finally, a marked positive shift of the reduction potential of CO₂ dissolved in CH₃CN, with respect to bare glassy carbon and to Pt electrodes, has been reported in the case of Fe-bipyridine-based metallopolymer deriving from oxidation of compound 5 [74].

The literature dealing with metal PTh-NP composites is more abundant, with respect to both fundamental and applicative studies, even addressed to the development of proper devices. In any cases, as to fundamental studies, PTh-NP composites have been considered in order to develop new electrocatalysts consisting of different metals. In particular, the electrooxidation of species such as methanol [223,231,246,244,245,250,252], formic acid [228,233,267], hydrogen [215,232,252] and ethylene glycol [365] has been studied, owing to the importance of these species as potential fuels. In addition, the electroreduction of oxygen [219,234,238], which constitutes the typical reducible species at the cathode in similar systems, has been investigated. Some authors also proposed the use of PTh-NP composites for the reduction of hydrogen ion to gaseous hydrogen, to be used as fuel [215,227]. Hydrogen ion can not be either oxidized or reduced on the surface of the pristine PTh, so that the presence of metal catalyst under the form of NPs is essential. Pt NPs have been traditionally used as catalysts, since they demonstrated to be highly active [186,187]. The high cost of Pt metal, and the need to improve further the catalytic activity and fouling resistance, have led to the development of bimetallic NP systems containing Pt, such as Pt-Ru [245,252,365], Pt-Pb [233], Pt-Sn [223], Pt-Pd [267], Pt-Ag [215]. The exact nature of these systems is often unknown. In addition, other Pt-free systems, such as Pd [219] and Ni/NiP [227] NPs, have also been tested.

As to the polymeric matrix, PTh [234,267,233], P3MT [215,219,222,223,246], PEDOT-PSS [238,245,250,252], PEDOT-polyvinylsulphate [252], polypyrrole-PTh copolymer [231] and PTh-coated multiwall carbon nanotubes [365] have been employed. The different polymers have been synthesized aiming at obtaining materials possessing high surface area and being mechanically, chemically and electrochemically stable in the operative conditions. Hence, these studies are normally carried out in strongly acidic media [223,231,246,244, 245,250,252], although some examples in neutral media [227,233] are reported. PSS and polyvinylsulphate also guarantee proton conductivity, as detailed in the following. The concentration of the electroactive species is normally very high - ca. 0.1-1 M. The mechanisms of the electrocatalytic reactions depend on a large number of parameters, such as the nature of the electroactive species, of the supporting electrolyte and of the NPs; in most cases the role of the components different from Pt is poorly understood. The tests are carried out using a planar electrode coated by the composites. Some authors [250,252] employed electrodes more similar to those used in fuel cells, such as gas diffusion electrode [364]. The results are often compared with those obtained with 'ideal' systems based on planar, metallic electrodes, even modified by deposition of a second metal.

As to actually usable devices, PTh-NP composites have been employed for the fabrication both of the anode and of the cathode sides of innovative low temperature fuel cells, in particular of Direct Methanol Fuel Cells (DMFCs). Although the various types of DMFCs can be significantly different from one another, the anode side traditionally consists

of finely divided Pt-Ru bimetallic NPs, which act as catalysts for the oxidation reaction; the NPs are dispersed on the surface of carbon black particles which, in turn, are supported on a polymeric matrix. These three components are deposited on a suitable electrode. The cathode side is similar, but Pt NPs are used as the catalyst for the reduction reaction. Carbon black guarantees electrical conductivity between the NPs and the supporting electrode, although it does not allow proton migration and limits the diffusion of gases and water. Hence, the polymeric matrix consists of a porous proton conducting polymer, such as Nafion[®].

PTh derivatives and, in particular, PEDOT-PSS, could replace, in principle, both carbon black and the proton conductor polymer [238,244-246,250,252]. In particular, systems based on PEDOT/PSS possess many advantages: the polymer is both electrically and proton conductive, thanks to the presence of PTh chains and polyanionic species, respectively; in addition, it is highly porous, so that water and gases can easily diffuse through. It is chemically stable, and the highly expensive catalysts dispersed inside can be recovered and reused. Finally, the processing of the material and the fabrication of the fuel cell stack is relatively simple.

In most cases, PThs embedding Pt under the form of NPs is used for both anode and cathode side, although some investigations on Pt-Ru bimetallic NPs have been performed [245]. NPs are deposited onto the PEDOT/PSS surface by chemical methods, such as reduction of Pt salts in the presence of formaldehyde [238,245,246,250], or by electrodeposition [244,245].

As to the fuel cell performance, this relatively new class of materials seems very promising, although literature reports rather scattered results for the DMFCs based on NP-PEDOT/PSS composites. The difficulty in properly utilising the catalysts constitutes the main problem: a fraction of the NPs seems to be electrically insulated from the supporting electrode, or partially fouled. Moreover, the access of the oxidisable and reducible species to the NP surface seems to be partially hindered. It is evident that further studies are necessary in order to improve the long-term stability, to optimise the performance, and to further reduce the loading of the expensive catalysts. Some authors [250] suggest the possibility to increase the performance by a partial overoxidation of the polymeric matrix, which probably leads to an increase of the porosity and to a change in the chemical nature of the film, although resulting detrimental in terms of electrical conductivity.

7.5. Charge Storage

Composite materials based on CPs and metal oxides constitute state-of-the-art compounds with recognized technological implications. In the area of energy conversion and storage, these materials have been applied as electrodes for batteries and for supercapacitors, as the high number of patents testifies.

Composites of PEDOT and layered vanadium oxides offer great advantages in battery applications with respect to both pristine materials [306,307,309,310]. It is known that the anion intercalation-deintercalation taking place during cycling of p-doped CPs is detrimental to the energy density of a cell with cation-generating lithium anodes. On the other hand, V₂O₅ is a well known good material for rechargeable Li⁺ batteries, but its reduction during discharge, accompanied by Li⁺ insertion, represents a rate limiting step. The use of CPs as intercalants can change the interlayer spacing of layered materials, enhancing the rate of Li⁺

migration. The composites display higher discharge capacities and reversibility for Li^+ insertion, than those observed for V_2O_5 alone.

Electrochemical supercapacitors represent a different and complementary approach to batteries for the storage of charge, allowing for higher power density but lower energy density than batteries. A supercapacitor is defined as an electrochemical capacitor possessing a large specific capacitance: it is based on materials possessing both large specific surface area and the capability to be reversibly oxidised or reduced over a wide potential range. Supercapacitors based on pristine CPs can deliver high specific power for a short time, though with significantly lower energy density than batteries. On the other hand, composites consisting of CPs and POMs are excellent materials for the fabrication of electrochemical supercapacitors, when combined with acidic electrolytes. This is due to several factors: CP acts as a stable and conductive matrix for the fast outer-sphere electron transfer occurring in correspondence to the POM redox sites immobilised inside the polymeric material; moreover, nanometric inorganic clusters can be introduced into the CP at a fairly high concentration level. Thus, the distance between the heteropolyanions mixed-valence redox centres is small enough to assure fast electron hopping between them. In addition, the use of these hybrids in electrochemical cells with acidic electrolyte membranes leads to a remarkable improvement in their behaviour to repeated cycles, thanks to the reversible reduction processes with concomitant protonation of POMs. PEDOT/ phosphododecanemolybdic acid composites have been efficiently used in developing supercapacitors [299,300,305]. Other composites have been proposed for the same purposes. Composite materials obtained depositing ruthenium oxide on PEDOT possessing high specific surface area are promising candidates for electrochemical capacitors of high quality [323,324]. Finally, the intercalation of PEDOT to MoO_3 or V_2O_5 foils produces an interesting increase of the double layer capacitance of pristine oxides [312,313], which suggests that these materials are also promising electrode materials for supercapacitors.

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