

## Redox-Active Metal-Organic Nanostructure Polymers and Their Remarkable Electrochemical Behavior

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### Abstract

A number of redox-active coordination polymers (CPs) or metal-organic frameworks (MOFs) have been successfully synthesized using transition metals and bridging ligands. This article aims to deal with gathering the aforementioned disperse issues regarding the electroactive CPs. It also goes towards illustrating the effects of various factors on the electrochemical behavior of CPs including nature of the ligand and its substitutes, metal centers, nanoporous coordination cages, coordinating atoms, solvent and temperature. Electrochemical investigations of CPs could bring insights into metal interactions and electronic communications caused by  $\pi$ -conjugated backbone insights into metal interactions and electronic communications caused by  $\pi$ -conjugated backbone of the bridging ligand. Furthermore, some fundamental aspects of electrochemistry and a few interesting applications of CPs will be addressed in this paper.

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### 1. Introduction

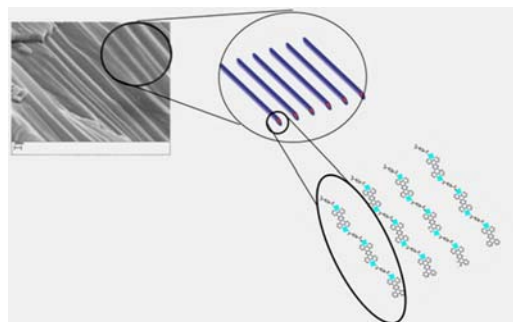
Electrochemistry is the study of chemical changes and flows of electrons typically between an electrode and a conductive solution known as electrolyte. Electrochemical processes have various applications in sensors, molecular electronics and both physical and chemical mechanisms. It is well established that many important reactions such as nucleophilic substitutions, metal hydride reductions, and

cycloadditions can be based on electron transfer processes [1].

Electrochemistry is applied in various fields of inorganic chemistry including coordination chemistry, organometallics, material science and biomimetics. In inorganic electrochemistry the main target of an electrochemical experiment is to investigate framework changes of inorganic compounds upon electron addition/removal.

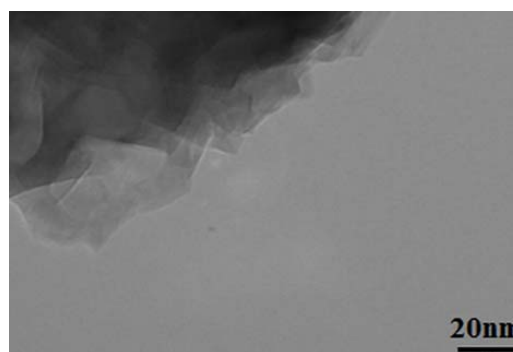
The bonding, anti-bonding or non-bonding character of the frontier orbitals of the molecules influences the structural alteration caused by electron exchanges [2].

On passing from mononuclear to polynuclear transition metal complexes, one can find properties related to not only metal-based components but also structure and composition of the whole array. A proper selection of the mononuclear building blocks and bridging ligands as well as an appropriate design of the structure can afford the occurrence of fascinating and potentially worthwhile processes such as energy transfer along predetermined pathways, photo-induced charge separation, and multi-electron exchanges at a particular potential. The metal-ligand coordination bonds have been vastly utilized to organize molecular building blocks into diverse supramolecular structures making use of directionality related to metal ions [3, 4]. The non-molecular compounds consisting of metal ions and inorganic ligands which their assembly leads to one-, two-, and three-dimensional networks are commonly known as coordination polymers (CPs) [5]. Recently, we investigated tetrapyrrophenazine ligand and its novel 1-D metal-organic wave-like CP of Ni(II) ion as well as a 2-D zinc metal-organic framework (MOF) (Fig. 1) [6, 7]. Apart from metal-ligand coordination bonds, there are some weak interactions such as hydrogen bonding,  $\pi \dots \pi$  or  $\text{CH} \dots \pi$  stackings, van der Waals contacts or their combinations that influence the design of



**Fig. 1.** Scanning electron micrograph (SEM) of  $[\text{Ni}_2(\mu_2\text{-tpphz})(\mu_2\text{-tp})(\text{H}_2\text{O})_6]_n \cdot (\text{tp}) \cdot 3.65(\text{H}_2\text{O})$  and schematic representation of nano-sized 1-D crystal fragments [6].

CPs [8, 9]. For instance, we have so far studied the structures and bonding for a number of salts of metal (III) ions solvated by dimethyl sulfoxide ligands [10-14]. Moreover, we have reported two novel thermodynamically stable pseudo-polymorph  $[\text{cis-RhCl}_4(\text{DMSO-}\kappa\text{S})_2\text{K}]_n$ , and  $[\text{cis-RhCl}_4(\text{DMSO-}\kappa\text{S})_2\text{K} \cdot 3\text{H}_2\text{O}]_n$ , and compound  $[\text{trans-RhCl}_4(\text{DMSO-}\kappa\text{S})_2\text{K} \cdot 0.25\text{H}_2\text{O}]_n$ , showing 1D or 2D networks mediated by K-Cl non-covalent bonding. The 2-D network with nano-layered sheets for the last compound was also confirmed by means of TEM images and presented in Fig. 2 [15].



**Fig. 2.** TEM image of  $[\text{trans-RhCl}_4(\text{DMSO-}\kappa\text{S})_2\text{K} \cdot 0.25\text{H}_2\text{O}]_n$  [15].

Porous CPs or MOFs have recently

appealed to many researchers due to their ability to encapsulate small molecules in their nanosized coordination cages [16, 17]. The final structures of MOFs can be influenced by multiple factors such as coordination geometry of the metals, solvent system, nature of the ligands, metal-to-ligand ratio, pH value, counter ions and temperature [18-21].

Among the numerous properties offered by nanoporous MOFs, redox activity has recently deserved special attention. Indeed, mixed valence compounds can show high electronic conduction [22-25], whereas solids stable upon redox reactions [26-27] can improve hydrogen sorption [28-31] or can be used as anode electrodes for lithium ion batteries [32-34] or for sensing through guest-network charge-transfer interactions [35, 36]. Moreover, many chemists devoted their attention to magnetism, luminescent, and electrochromism properties of non-porous CPs [37, 38].

A wealth of information can be obtained from electrochemical investigations of CPs. If the ligand is redox active, a combination of the redox properties of the ligand and the metal is considered to provide a multi redox system. Knowing electrochemical behavior of CPs helps chemists to understand whether redox process is centered on the metal or polytopic ligands. It also assesses electrochemical interactions between vicinal metallic ions and reversibility of redox-active species [39].

The knowledge on the redox properties of CPs is rapidly accumulating, but it is

disperse in a great number of journals. We have made an attempt to collect some of the available results, and we present them together with some fundamental introductory concepts and a few interesting applications.

## 2. Cyclic voltammetry (CV)

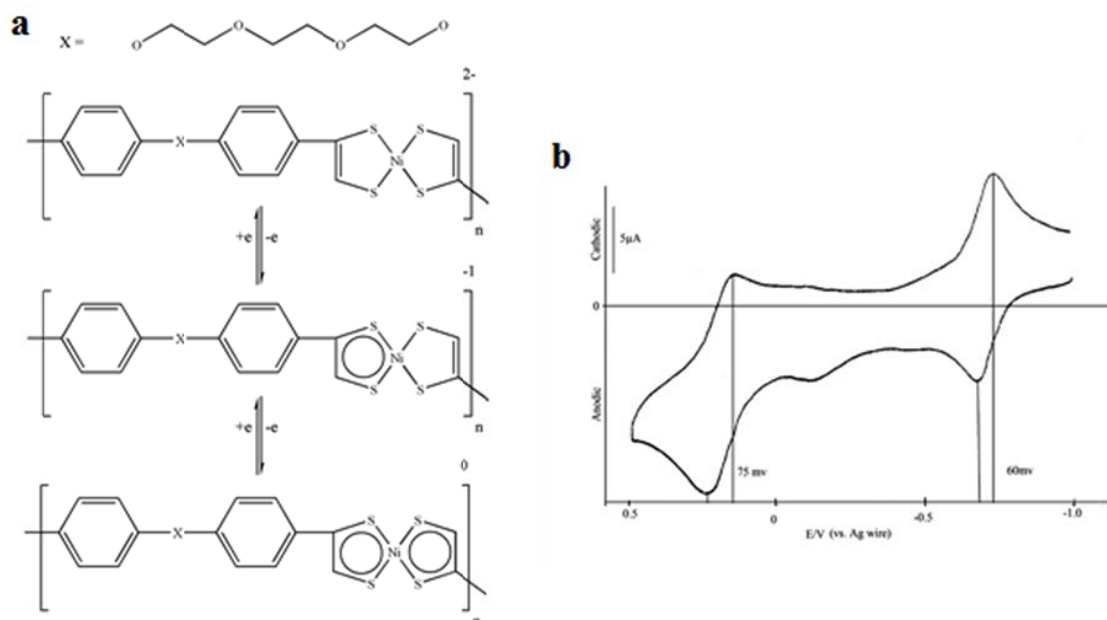
Voltammetric techniques are based on a change in the potential of working electrode and observation of the generated current as a function of time (or in some cases, imposing a current and observing the potential) [2]. These techniques have been utilized for the study of electrochemical reactions [40], electrochemically generated free radicals [41], coordination chemistry [42], solar energy conversion [43], and determination of trace concentrations of biologically and clinically important compounds [44, 45].

Among nonstripping voltammetric forms [46], cyclic voltammetry (CV) is the most popular voltammetric technique in the field of inorganic chemistry. A lot of information will be obtained from a cyclic voltammogram such as peak potential ( $E_p$ ), current of the peaks ( $i_p$ ) with respect to their baseline and peak-to-peak separation ( $\Delta E_p$ ). For any process the ratio between the current of the reverse and forward peak,  $i_{pr}/i_{pf}$ , is particularly important. Chemical reversibility of an electrode reaction can be judged based on this current ratio. If the reaction is reversible then the separation of the peak potentials,  $\Delta E_p$ , will be close to  $58/n$  mV (at 25°C) meaning that redox step isn't accompanied by important structural reorganization [2, 47].

Consider the following example that illustrates two separate redox processes for polymeric nickel bis(dithiolene) complex shown in fig. 3a [48]. A cyclic current-voltage curve (voltammogram) of the polymer is depicted in fig. 3b to clarify the electrochemical behavior of the polymer.

As the potential is scanned the current rises to a peak and then decays. The current depends on the movement of electroactive materials to the surface of the electrode and the electron transfer reaction. At potentials equal to  $-0.8\text{V}$  the polymer complex remains in the dianionic state and then exhibits two

redox processes at  $E_{1/2} = -0.71\text{V}$  and  $E_{1/2} = +0.19\text{V}$  (vs. Ag wire) while scanning anodically. These two processes are reversible as evident by the 60 and 75mV peak-to-peak separation seen for each process, respectively. Referring to fig. 3a, these redox processes were attributed to the reversible oxidation of dianion to monoanion and finally to the neutral state. Redox couples whose peaks shift farther apart with increasing scan rate are characterized as quasi-reversible.



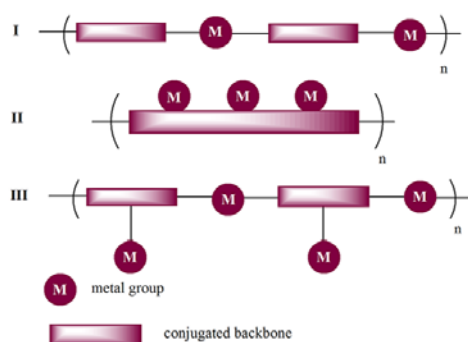
**Fig. 3.** (a) Redox process of polymeric nickel bis(dithiolene) (b) cyclic voltammogram for the polymer on a carbon working electrode in a 0.1 M TBAClO<sub>4</sub>/DMF solution [48].

By quasi-reversible, electrochemists mean that some important structural changes occurred during the redox process but the framework does not undergo fragmentation [2, 47].

In this connection, electrochemical voltammogram of coordination polymer [AgL]<sub>n</sub> (HL = 1H-1,2,4-triazole-1-

methylene-1H-benzimidazole-1-acetic acid) in water containing 0.05 molL<sup>-1</sup> KCl showed one pair of oxidation–reduction peaks corresponding to the redox couple of Ag(II)/Ag(I) [49]. Peak potentials were  $E_{pa} = 0.162\text{V}$  and  $E_{pc} = 0.025\text{V}$  (vs. Ag/AgCl), the average formal potential [ $E_{1/2} = (E_{pa} + E_{pc})/2$ ] was 0.0935 V, the peak-to-peak

separation between the anodic and cathodic peaks ( $\Delta E_p$ ) was 0.137 V and the ratio of the peak currents ( $i_{pc}/i_{pa}$ ) was 1.66. These features are indicative of a quasi-reversible electrode process. There are some cases in which the peaks are so widely separated that no parts of the two peaks overlap on the potential axis at all. These are generally known as totally “irreversible” systems. These reactions yield the products that can't be recycled electrochemically to give back the original reactants [47].



**Fig.4.** Model systems for metal-organic frameworks [55, 56].

### 3. Electroactive coordination polymers

Polymeric nanostructures and molecules with  $\pi$ -conjugated systems that possess redox active properties have attracted a widespread interest. A distinctive feature of these conjugated materials is electronic communication via transition metals'

interactions through  $\pi$ -conjugated backbone [50-53]. Redox properties of both electroactive ligands and the metals are extremely important to develop a multi-redox system [54]. Metal-contained conjugated oligomers and polymers have been previously reviewed by Wolf Mo. [55] and Moonhyun Oh. [56]. As it is evident in fig. 4, in the case of both metals and ligands possessing two coordination sites, these compounds are arrayed alternatively to give the corresponding MOF with linear structure (type I). Another designed system is produced by a  $\pi$ -conjugated ligand with multiple-coordination sites giving a multi-nuclear compound (type II). Appropriate organometallic  $\pi$ -complexes are also able to function as linkers or spacers to afford metal-organometallic coordination networks (type III). From the viewpoint mentioned above, some of the redox-active  $\pi$ -conjugated ligands are listed in table 1.

Also, it was emphasized that it is hard to characterize most unfunctionalized polymers due to their poor solubility when the samples are needed as a solution form [61]. Thus, modified carbon paste electrodes can be fabricated as the working/indicator electrodes for electrochemical investigations.

**Table 1.** Redox states of some  $\pi$ -conjugated bridge ligands

Redox states		References
<p>Hydroquinone dianions</p> <p>Semiquinone radical anion</p> <p>Quinone</p>	$\xrightleftharpoons{+e}$ $\xrightleftharpoons{-e}$	54
<p>Tetrathiafulvalene (TTF)</p>	$\xrightleftharpoons{+e}$ $\xrightleftharpoons{-e}$	57
<p>Pemigraniline</p> <p>Emeraldine</p> <p>Leucoemeraldine</p>	$\xrightleftharpoons{2e, 2H^+}$	54
<p>2,4-ditert-butyl-6-(phenylimino) phenolate</p> <p>2,4-ditert-butyl-6 (phenylimino) semiquinonate</p>	$\xrightarrow{-e}$ $\xrightarrow{-e}$	58
<p>9,10-phenanthrene diimine</p> <p>diimino-semiquinonate</p> <p>phenanthrene diamide</p>	$\xrightarrow{+e}$ $\xrightarrow{+e}$	59
<p>1,2,4,5-tetracyanobenzene (TCNB)</p> <p>TCNB•<sup>-</sup></p>	$\xrightleftharpoons{+e}$	60

Table 2 presents electrochemical data for some reported CPs. The abbreviations used for the ligands, solvents, etc. are shown in section 6.

A great deal of information can be obtained from electrochemical investigations of redox-active MOFs. Different factors can influence redox potential of these systems such as ligand substitutes, metal centers,

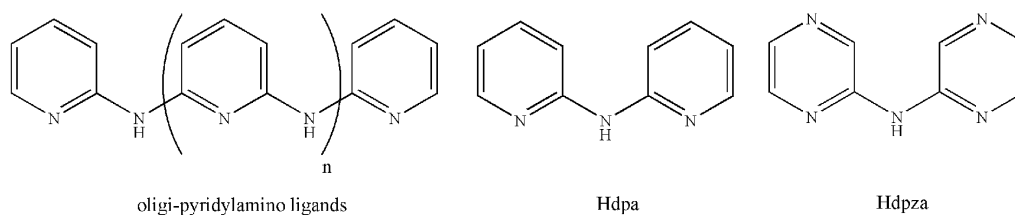
nanoporous coordination cages, coordinating atoms, solvent and temperature. In this paper, we will briefly discuss the effect of these factors on the electrochemical properties of CPs.

### 3.1. Ligand's influence on the redox properties

A survey of electroactive coordination polymers revealed that the size of nanopores, nature of the substitutes on ligands,  $\sigma$ -donor effects, and  $\pi$ -back bonding interactions influence their redox behavior [68, 71-73]. For instance, Megumu Munakata [60] prepared polymeric coordination compound  $[\text{Cu}_2(\text{TCNB})_3](\text{PF}_6)_2(\text{Me}_2\text{CO})_4$ , using  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  and 1,2,4,5-tetracyanobenzene (TCNB). Solutions of acetone were employed for cyclic voltammetric measurements vs. Ag/AgCl. The polymer exhibited a quasi-reversible one-electron reduction corresponding to the electron transfer from Cu(I) to the electron acceptor ligand.

Electron transfer from Cu(I) to TCNB ligand has been confirmed by the presence of an EPR signal for this polymer. The reduction potential of -0.55V is close to that of noncoordinated TCNB (-0.49V), suggesting that the  $\pi$ -back bonding interactions almost thoroughly compensate the  $\sigma$  donor effect of the ligand.

C.-Y. Cao et al. [71] have made use of the bidentate ferrocenyl sandwich molecule N,N'-bis-3-pyridylmethyl-1,1'-ferrocenedicarboxamide (3-BPMFA) as an organometallic coordination ligand in the reaction with  $\text{CdBr}_2$  to construct coordination polymers. They prepared the solvated polymer  $[\text{Cd}(\mu\text{-3-BPMAF})_2\text{Br}_2]_n \cdot n\text{MeOH}$  from methanol and unsolvated one  $[\text{Cd}(\text{3-BPMFA})(\mu\text{-Br})_2]$  from DMF- $\text{Et}_2\text{O}$ . The electrochemical behavior of 3-BPMFA ligand and the polymers was investigated in DMF by differential pulse voltammetry. Iron redox peak of 3-BPMFA ( $E_p=0.784\text{V}$ ) corresponds to a single ferrocene/ferrocenium redox ( $\text{Fc}/\text{Fc}^+$ ) couple. In comparison with unsubstituted ferrocene ( $E_p=0.456\text{V}$ ), this redox peak shifted towards more positive values. This can be related to the electron-withdrawing substituted groups of ferrocene that decrease the density of cyclopentadienyl ring and make the ferrocene unit more difficult to oxidize. By employing oligo- $\alpha$ -pyridylamino ligands (scheme 1), a series of extended metal atom chains (EMACs) have been synthesized. H. H Ismayilov [72] made great efforts to use the variety of metals and extend lengths of the EMACs. They included pyrazine instead of pyridine rings in oligo- $\alpha$ -pyridylamino ligand.



**Scheme 1.** Pyridylamino ligands [72].

**Table 2.** Electrochemical data for some of the reported coordination polymers.<sup>a</sup>

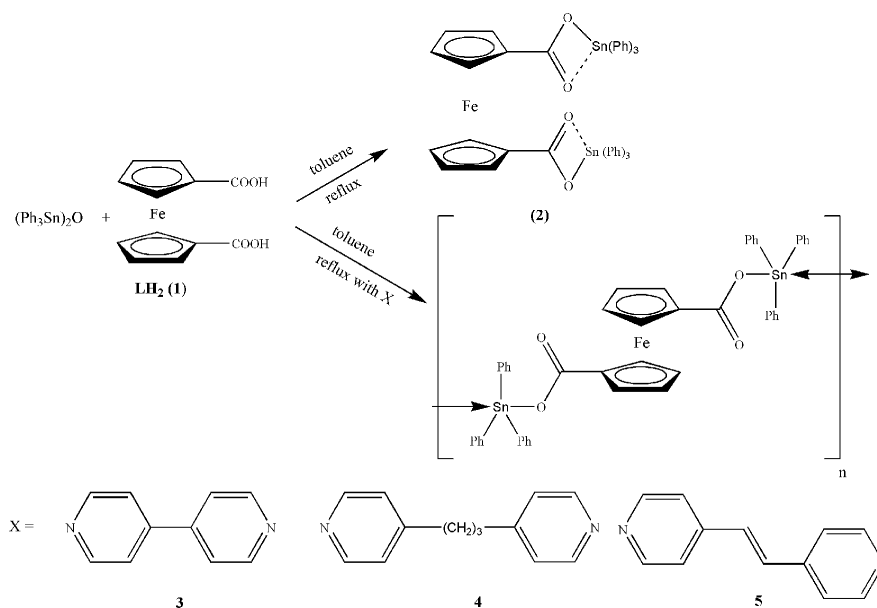
Coordination polymer	Method	Solvent	Reference electrode	Working electrode	Ligand-centered data, V	Metal-centered data, V	Reference
[Cu <sub>2</sub> (TCNB) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub> (Me <sub>2</sub> CO) <sub>4</sub>	CV	Me <sub>2</sub> CO	Ag/AgCl	Pt	-0.55q	+0.5i <sub>7</sub> , +0.65i <sub>1</sub> (Cu <sup>III</sup> and existing Cu <sup>II</sup> )	60
[Co(3-BPCB)(1,3-BDC)].H <sub>2</sub> O	CV	-	SCE	modified carbon paste electrode (CPE)	-	0.509r (Co <sup>III</sup> )	62
[Cu(4-BPCB)] <sub>2</sub> .0.5(4-BPCB)	CV	-	SEC	CPE	-	0.494r (Cu <sup>II/I</sup> )	62
{Zn(FeCOO) <sub>2</sub> (BBBM)}.H <sub>2</sub> O <sub>n</sub>	DPV	DMF	SCE	Pt	-	+0.710 (Fe <sup>II/III</sup> )	63
[La(μ <sub>2</sub> -OOCH <sub>4</sub> C <sub>6</sub> Fc)(η <sup>2</sup> -OOCH <sub>4</sub> C <sub>6</sub> Fc)(CH <sub>3</sub> OH)] <sub>n</sub>	DPV	DMF	Ag/AgCl	Glassy carbon (GC)	-	+0.577r (Fe <sup>IV/III</sup> )	64
[Pr(μ <sub>2</sub> -OOCH <sub>4</sub> C <sub>6</sub> Fc)(η <sup>2</sup> -OOCH <sub>4</sub> C <sub>6</sub> Fc)(CH <sub>3</sub> OH)] <sub>n</sub>	DPV	DMF	Ag/AgCl	GC	-	+0.575r (Fe <sup>IV/III</sup> )	64
[Nd(μ <sub>2</sub> -OOCH <sub>4</sub> C <sub>6</sub> Fc)(η <sup>2</sup> -OOCH <sub>4</sub> C <sub>6</sub> Fc)(CH <sub>3</sub> OH)] <sub>n</sub>	CV	DMF	Ag/AgCl	GC	-	+0.576r (Fe <sup>IV/III</sup> )	64
[(1,8-bis(2-methylthioethoxy)antraquinone)Ag]BF <sub>4</sub>	CV	CH <sub>3</sub> CN	SCE	Pt	-1.019r, -1.335r	+0.280i (Ag <sup>0/I</sup> )	65
[Cu(PDIP)(1,4-BDC)]	CV	-	SCE	CPE	-	-0.305q (Cu <sup>II/I</sup> )	77
[Cu <sub>4</sub> (2,2,2,2-[2,5-dimethyl-1,4-phenylenebis(methylenenitrilo)]tetraacetate)(H <sub>2</sub> O) <sub>8</sub> ]4H <sub>2</sub> O <sub>n</sub>	CV	-	SCE	GC	-	-0.400r (Cu <sup>II/I</sup> )	66
[AgL] <sub>n</sub> (HL = 1H-1,2,4-triazol-1-methylene-1H-benzimidazole-1-acetic acid)	CV	H <sub>2</sub> O	Ag/AgCl	GC	-	+0.094q (Ag <sup>II/I</sup> )	49
[1,5-bis(2-methylthioethoxy)antraquinone).Ag.CH <sub>3</sub> CN]BF <sub>4</sub>	CV	DMF	SCE	Pt	-0.99r, -1.365r	+0.258r (Ag <sup>0/I</sup> )	65
{[Cu <sup>II</sup> (phen)(SSA) <sub>2</sub> Cl <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub> (DMF) <sub>2</sub> ] <sub>n</sub>	CV	DMF	SCE	GC	-	+0.0615q (Cu <sup>II/I</sup> )	67
PDP[Cu <sup>I</sup> PDP] <sub>n</sub> (BF <sub>4</sub> ) <sub>n</sub>	CV	-	Ag/AgCl	ITO	-	+1.1 (Cu <sup>I/II</sup> )	68
[(Me <sub>3</sub> Sn) <sub>2</sub> L] <sub>n</sub> L = 4,4'-bipyridine	CV	CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	BAS Pt disk	-	+0.81q (Fe <sup>IV/III</sup> )	69
[(Me <sub>3</sub> Sn) <sub>2</sub> L] <sub>n</sub> L = 4,4'-trimethylenebipyridine	CV	CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	BAS Pt disk	-	+0.72i (Fe <sup>IV/III</sup> )	69
[(Me <sub>3</sub> Sn) <sub>2</sub> L] <sub>n</sub> L = 4,4'-vinylenebipyridine	CV	CH <sub>2</sub> Cl <sub>2</sub>	Ag/AgCl	BAS Pt disk	-	+0.75q (Fe <sup>IV/III</sup> )	69
[{Cu(mebpa)} <sub>2</sub> β-Mo <sub>8</sub> O <sub>26</sub> ]	CV	-	Ag/AgCl	CPE	+0.158r -0.094r +0.344r (Mo <sub>8</sub> O <sub>26</sub> <sup>4-</sup> reduction)	-	70
[bis-terpyridine-Co-dicyclam-Cu] <sub>n</sub> <sup>2n+</sup>	CV	DMF	(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe/ (C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe <sup>+</sup>	Vitreous carbon disk	-2.090	-1.140(Co <sup>III</sup> ), -1.520(Cu <sup>II/I</sup> ), +0.510 (Cu <sup>III/II</sup> ), -0.225(Co <sup>III/II</sup> )	39

<sup>a</sup> i = irreversible; q = quasi-reversible; r = reversible



The introduction of one or more of the nitrogen-rich aromatic rings such as pyrazine to the ligand revealed very different redox properties. For instance, electrochemical studies in trinuclear extended metal atom chains of  $[\text{Cr}_3(\mu_3\text{-dpza})_4\text{Cl}_2]$  and  $[\text{Cr}_3(\mu_3\text{-dpa})_4\text{Cl}_2]$  showed that existence of the pyrazine rings in the

complex facilitated reduction and retarded oxidation. This observation is sensible in the view of the fact that pyrazine ring with two nitrogen atoms is more electronegative than the pyridine ring.



**Scheme 2.** Organo-tin coordination compound [69].

Redox potentials of MOFs have been affected by coordinating atoms. Let's consider electrochemistry of the CPs reported by V.Chandrasekhar and R.Thirumoorthi [69]. First they obtained a molecular dinuclear organotinocarboxylate  $(\text{ph}_3\text{Sn})_2\text{L}$  (2) in the condensation reaction between  $\text{LH}_2$  (1) and bis(triphenyltin) oxide. They took advantage of unsaturated coordination site in complex (2) to prepare one-dimensional polymeric compounds 1-3 in the presence of ditopic ligands (scheme 2). Electrochemical studies of these ferrocene-tin hybrid systems were carried out in  $\text{CH}_2\text{Cl}_2$  containing  $[\text{n-Bu}_4\text{N}][\text{PF}_6]$  at a

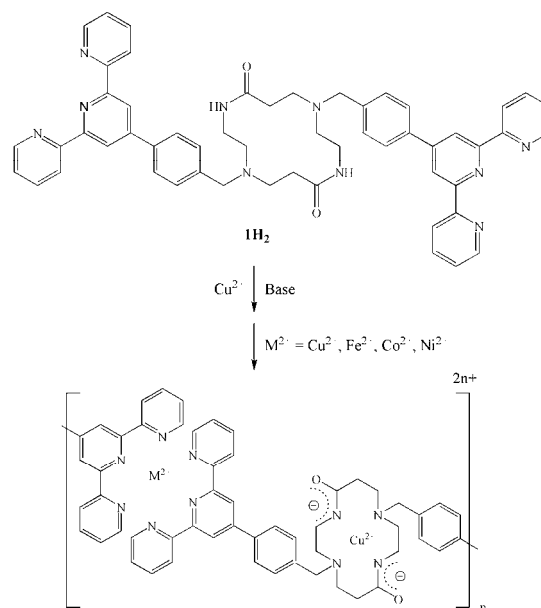
scan rate of 100mV/s (vs. Ag/AgCl). The main characteristic of these compounds was their electrochemical stability even after 6 cycles. Compounds 1 and 3 revealed a single quasi-reversible peak due to an oxidation at +0.81 and +0.75V, respectively while compound 2 showed a single irreversible peak at +0.72V. These polymers are easier to oxidize than the parent compound 2 because of the coordination of the nitrogen atom to tin center.

Functionalizing and lengthening the organic linker units can lead to MOF structures with the same crystallographic space group but different pore sizes. A. Liu et al. [73] prepared nanoporous CP

multilayers of Pd(II) using six kinds of multidentate ligands as linkers. Electrochemical studies were performed using Pt wire as the auxiliary and Ag/AgCl as the reference electrode. The ITO electrode coated with the CPs and used as the working electrode in KCl electrolyte containing  $K_3[Fe(CN)_6]$ . Different current intensity was observed depending on the penetration of electroactive  $Fe(CN)_6^{3-/4-}$  molecules through CP multilayers. The results showed significant decrease of the current peak for the CPs with small nanoporous coordination cages.

### 3.2. Metal centers and electrochemical properties

The nature of the ligand, the distance between metal centers and the  $d^n$  electron configuration determine the redox potential of the polymeric system. As a typical example Gasnier et al. [39] described the preparation of homo- and heterometallic CPs containing dioxocyclam ligand (dioxocyclam=1,4,8,11-tetraazacyclo-tetradecane-5,7-dione) and transition metal cations ( $M^{2+} = Cu^{+2}, Fe^{2+}, Co^{2+}$  and  $Ni^{2+}$  ions). The ligand and the structure of its coordination polymer are shown in fig. 5. Electrochemical characterization of the polymer was performed by cyclic voltammetry in DMF containing tetra-n-butylammonium perchlorate (TBAP, 0.1M) electrolyte. In the case of  $M^{2+} = Co^{2+}$ , oxidation and reduction potentials were close to nonpolymeric complex of dioxocyclam ligand with  $Cu^{2+}$  and  $Co^{2+}$ .



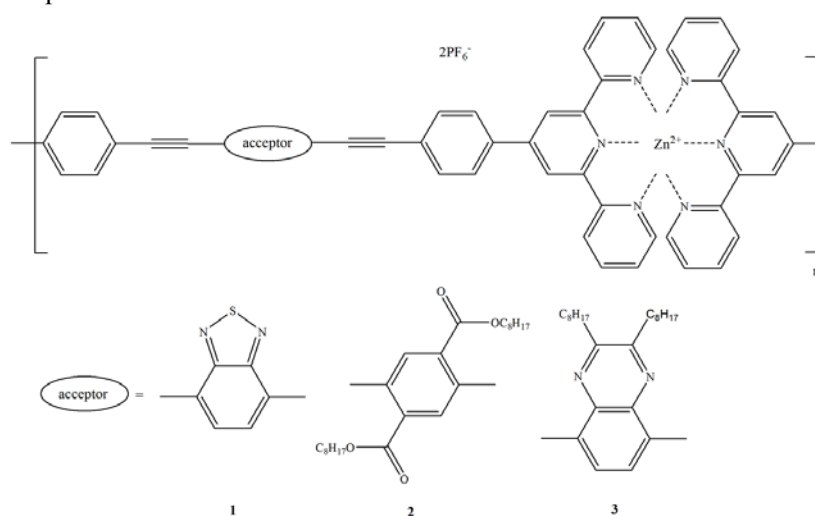
**Fig. 5.** Schematic preparation of polymer species  $1CuM$  ( $M = Fe, Co, Ni$  or  $Cu$ ) [39].

These data confirmed that the redox active units in the polymer chain behave as if they are almost independent and there are none or only very weak electrochemical interactions between two vicinal metallic ions because of non-conjugated nature of the ligand.

Schlütter et al. [74] reported a series of rigid  $\pi$ -conjugated bis(terpyridines) containing electron acceptor spacer units. These units were applied for the self-assembly reaction with  $Zn^{II}$  ions to form metallopolymers (Fig. 6). All polymers exhibited quasi-reversible reduction peaks. For example polymer 3 which was coated on Pt wires, showed two peaks at -1.29V and -1.62V (vs.  $Ag/Ag^+$ ). The waves were related to the reduction of the terpyridine moiety and the attached  $\pi$ -conjugated spacer units inside the polymers. Since  $d^{10}$  electron configuration of the  $Zn^{II}$  metal centers is stable, no significant oxidation process was observed up to +1.5V. B.-Q Liu et al. [64]

prepared a series of *m*-ferrocenylbenzoate [m-NaOOCH<sub>4</sub>C<sub>6</sub>Fc, Fc=( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)] lanthanide CPs by slowly diffusing a methanol solution of *m*-ferrocenylbenzoate sodium into a water solution of Ln(NO<sub>3</sub>)<sub>3</sub>.nH<sub>2</sub>O. They found that lanthanide ions, the phenyl ring and carboxylate groups influenced the oxidation potentials of the polymers. CV and DPV voltammograms revealed that E<sub>1/2</sub> potentials of the CPs were slightly more positive than that of *m*-

HOOCH<sub>4</sub>C<sub>6</sub>Fc. It is evident that the electron-withdrawing nature of the coordinated lanthanide ions in the polymers causes the oxidation of the ferrocenyl moieties to be difficult. However, the minor change in the potential in the presence of lanthanide ions implied that the ions have a small influence on the oxidation of the ferrocenyl moieties in the polymers because of relatively long charge-transfer distance



**Fig. 6.** Schematic representation of Zinc (II)-containing metallopolymers [74].

between the lanthanide ions and Fe<sup>II</sup> ion by carboxylate group, phenyl ring and cyclopentadienyle.

### 3. 3. Effect of temperature on the potential

Separation between potentials of the forward and reverse peaks (peak-to-peak separation),  $\Delta E_p$ , is related to the electrochemical reversibility of an electrode reaction, namely the rate of the electron transfer. According to the equation (1)  $\Delta E_p = 2.3RT/nF$  (1)

$\Delta E_p$  is equal to  $59/n$  mV at 25°C and *n* is the number of electron exchanged per molecule of oxidant [2].

Regarding this, the electrochemical properties of C<sub>2</sub>Co<sub>2</sub> cluster-bridged bipyridine ligand [(3-C<sub>5</sub>H<sub>4</sub>NCO<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>C<sub>2</sub>Co<sub>2</sub>(CO)<sub>6</sub>] was investigated in DMF at different temperatures [75]. The CV voltammograms of the ligand were determined at both room and low temperature. The ligand displayed an irreversible reduction process at a peak potential of -1.36V and an irreversible oxidation process at potential of -0.23V at room temperature. The peak displayed at -

1.36V is attributed to the one-electron reduction of the cluster unit  $C_2Co_2(CO)_6$  and production of the corresponding radical anion which is fairly unstable and may decompose on the surface of an electrode to produce the  $Co(CO)_4^-$  monoanion with an irreversible one-electron oxidation process at -0.23V. However the irreversible reduction peak at -1.36V displayed at room temperature becomes reversible and the irreversible oxidation process at -0.23V disappears at low temperature, both indicating that the radical anion of the ligand becomes stable at such a low temperature.

### 3. 4. Scan rate effects

The rate of an electron transfer can be influenced by the rate with which the electrode is supplied with reagents and cleared from the electrogenerated products. Movements of electroactive species from the bulk of solution to the electrode surface are governed by three physical mechanisms: convection, diffusion, and migration. Diffusion occurs when there is a gradient of concentration in solution, migration is caused by a gradient of an electrical potential and convection induced by a mechanical force. Investigation of redox processes controlled only by diffusion is advantageous because the laws are thoroughly known to chemists [2]. Diffusion-controlled processes typically exhibit a peak current ( $i_p$ ) that is linearly dependent on the square root of the scan rate ( $v^{1/2}$ ), while surface-confined species exhibit  $i_p$  dependent on the scan rate ( $v$ ).

To further illustrate the role of the scan rate consider, for example, polymeric nickel

bis(dithiolene) compound mentioned in section 2 (Fig. 3). The observed linear dependence of  $i_p$  on  $v^{1/2}$  for both anodic and cathodic current between 40 and 200  $mVs^{-1}$  showed that the polymer does not deposit on the electrode surface at cathodic potentials of +0.5V. This redox behavior was in agreement with none polymeric nickel bis(dithiolene) complexes [76] showing that the metal center approaches the electrode surface close enough for electron transfer although the metal complexes are contained in the polymer network [48].

While nickel bis(dithiolene) polymer showed linear dependence of  $i_p$  on  $v^{1/2}$ , polymeric compound [Cu(PDIP)(1,4-bdc)] revealed dependence of  $i_p$  on the scan rate [77]. The polymer bulk-modified carbon paste electrode was fabricated as the working electrode. CV voltammogram in 0.1 M aqueous solution of acetate buffer (pH=3.3) showed a quasi-reversible reduction for  $Cu^{2+}/Cu^+$  at  $E_{1/2} = -305$  mV in the scan rate of 60  $mVs^{-1}$ . When the scan rate was increased from 60 to 450  $mVs^{-1}$ , the peak current showed dependence to  $v$ , therefore the redox process was surface-controlled; and the peak potentials changed gradually: the cathodic peak potentials shifted to negative direction and the corresponding anodic peak potentials shifted to positive direction while increasing the scan rate.

### 4. Applications of redox-active coordination polymers

Since many redox-active transition metal coordination compounds exhibit intense coloration due to metal-to-ligand charge transfer (MLCT), intervalence CT,

intraligand excitation, or visible region electronic transitions, they can be used as electrochromic materials. One of the main uses of electrochromic materials is in smart windows for cars and buildings. Fabrication of solid-state electrochromic devices generally requires polymeric systems although it is possible to make solution-phase devices with mononuclear transition metal compounds.

Electrochromism refers to the generation of different visible-region electronic absorption bands caused by switching between different redox states. In this case, the electrochemistry of  $\text{PDP}[\text{Cu}^{\text{I}}\text{PDP}]_n(\text{BF}_4)_n$  polymer (PDP=phenanthroline-dodecane-phenanthroline) is characterized by a Cu(I)/Cu(II) redox process at a formal potential value of 1.1V vs. Ag/AgCl [68]. The polymer showed the absorption peak at 455 nm that is related to an MLCT transition in the compound. Spectral changes of the polymer film on an ITO electrode were investigated by applying potentials of 0 or 1.4V vs. Ag/AgCl in 0.1M  $\text{LiClO}_4$  in ethanol-water. The disappearance of the absorption peak at 455 nm upon stepping the potential from 0 to 1.4V indicates the complete oxidation of the Cu(I) cluster to Cu(II) and disappearance of the absorption in the visible region. The authors have also pointed out that  $\text{TPP}[\text{Fe}^{\text{II}}\text{TPT}]_n(\text{PF}_6)_{2n}$  and  $\text{CTPCT}[\text{Fe}^{\text{II}}\text{CTPCT}]_n(\text{PF}_6)_{2n}$  exhibited a considerably enhanced switching rate.

Nguyen et al. [57] prepared three-dimensional porous CPs formulated as  $\text{M}_2(\text{TTF-TC})\text{H}_2$  (TTF-TC=tetrathiafulvalene tetracarboxylic acid, M=K, Rb, Cs). As shown in table 1, tetrathiafulvalene (TTF)

derivatives are sulfur-rich  $\pi$ -electron donors and can partially oxidize to form organic molecular conducting salts. Thus the authors took advantage of the redox activity of the organic linker as alternative electrode materials in lithium-ion batteries.

X.-L. Wang et al. [62] prepared MOF of  $[\text{Cu}(4\text{-bpcb})(1,3\text{-BDC})]_2 \cdot 0.5(4\text{-bpcb})$ , using N,N-bis (3-pyridinecarboxamide)-1,4-benzene(3-bpcb) and 1,3-benedicarboxylate ligands. The polymer possesses potential applications in the field of electrochemistry. The polymer carbon paste electrode (CPE) was fabricated as the working electrode due to insolubility of the compound in water and common organic solvents. The mean peak potential for the polymer-CPE was 494 mV (100mV/s) that was related to the redox couple of  $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ . The electrocatalytic reduction of nitrite was performed at both a bare CPE and the polymer CPE containing 1M solution of  $\text{H}_2\text{SO}_4$ . There was no redox peak at the bare CPE in the presence of nitrite. By increasing nitrite concentrations, the reduction peak currents increase noticeably and the corresponding oxidation peak currents decrease remarkably at the polymer-CPE. The results indicate that the polymer possesses good electrocatalytic activity toward the reduction of nitrite.

## 5. Conclusions and perspectives

Intense effort has been devoted to the design and controlled crystallization of coordination polymers and supramolecular nanostructures based on transition-metal ions and multifunctional bridging ligands owing to their potential applications. The

structures of assembled products are greatly affected by a variety of conditions, such as temperature, pH value, molar ratio of reactants and solvent system. Electroactive metal-contained conjugated polymers such as those described in this article exhibit interesting redox properties due to metal interactions and electronic communications provided by the  $\pi$ -conjugated backbone of the spacer ligand. The electronic exchange can be affected by the nature of the spacers and metals. Redox-active coordination polymers are excellent candidates for potential functional solid states materials and the development in this field will be strictly connected with a more use of modeling of structural designs and properties.

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