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Supramolecularly Organized Systems Based on Transition Metal Complexes with Schiff's Bases. Photo- and Electrochemical Activity

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SUMMARY: In the present paper we report about the last advances concerning the structure and properties of electrochromic photosensitive metallopolymers based on the complexes of Pt, Pd, Ni, Co, Cu with Schiff's bases. The criteria of selection of the object for the synthesis of new polymers with one-dimensional, reversible, controlled photo- and electroinduced charge transfer was determined. A model for the polymer structure was proposed. The ohmic resistance in the direction parallel and perpendicular to the microelectrode surface of gold-coated α-Al_2O_3 differs as 1 : 10^6-10^9 depending on the polymer and film thickness. A qualitative model of the processes of light energy accumulation was proposed.

Introduction

The progress of organized molecular systems chemistry on solid carriers opens new perspectives for the treatment of photosynthesis and catalysis topical problems$^{1)}$.

It has been found$^{2)}$ that polymers of homonuclear homoligand type based on transition metal complexes with Schiffs bases and 5-chloro-1,10-phenanthroline represent very convenient models for the investigation of long-range energy and electron transfer along the redox sites.

The photosensitive, photo- and electroactive, electrochromic polymers obtained exist in two stable forms: oxidized and reduced. This fact explains the good reversibility of the redox processes in the polymer under the action of electric and electromagnetic fields.

In this paper we report the structure and properties of the polymeric systems poly-[Msalen], poly-[Msalphen], poly-[Msalpn-1,3] and poly-[Msalpn-1,2] (M ≡ Ni(II), Pd(II), Pt(II), Cu(II), Co(III); salen, salphen, salpn-1,2 and salpn-1,3 - bis(salicylidene)-ethylenediamine, bis(salicylidene)-o-phenylenediamine, bis(salicylidene)-1,2-propylenediamine, bis(salicylidene)-1,3-propylenediamine respectively (Fig. 1).

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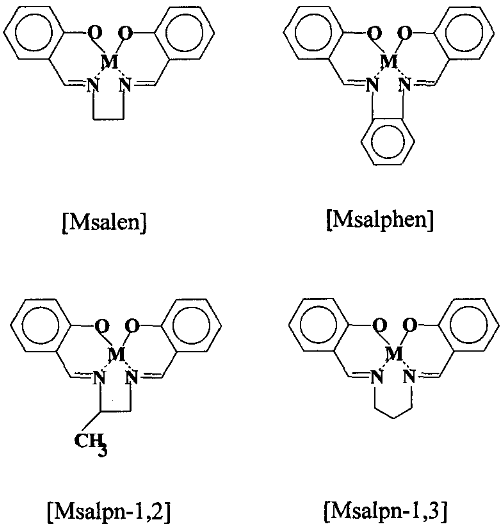

[Msalen] [Msalphen]

[Msalpn-1,2] [Msalpn-1,3]

Fig. 1: Complex formulas and abbreviations

Morphology

New polymers form on solid carriers by electrooxidation of 1 mM acetonitrile solutions of initial complex compounds by potentiostatic (Tab. 1) and potentiodynamic conditions[3]. These carriers were planar and wire electrodes made of glassy carbon, Au, Pt and optically transparent materials.

The following physico-chemical methods were used for the solution of the raised problems: cyclic voltammetry, electronic absorption spectroscopy, spectral-luminescence, X-ray photoelectronic spectroscopy and photoelectrochemistry.

A correlation between spectral and electrochemical characteristic parameters was discovered (Tab. 2). The criteria of selection of the object for the synthesis of the new polymers was determined.

The kinetic laws of polymer growth and the optimal conditions of electrochemical synthesis and behavior, i.e. temperature, light energy and intensity, electrolyte properties, electrochemical window, etc., were determined.

We have proposed the mechanism of formation of metallopolymers[3].

Tab. 1. Correlation spectral and electrochemical characteristics of complexes

Complex compounds	Potential of growth, V vs Ag/AgCl	MLCT absorption band, λ_{max} nm; (lg ε)
[Nisalphen]	1,00 -1,05	475 (4,16)
[Pdsalphen]	1,00 -1,05	460 (4,16)
[Nisalen]	1,05 -1,10	440 (3,46)
[Cusalphen]	1,05 -1,10	420 (4,16)
[Ptsalpn-1,3]	1,05 -1,10	420 (3,71)
[Ptsalpn-1,2]	1,05 -1,10	415 (3,78)
[Ptsalen]	1,05 -1,10	415 (3,75)
[Pdsalpn-1,3]	1,10	405 (3,41)
[Pdsalpn-1,2]	1,10	405 (3,88)
[Pdsalen]	1,10	400 (3,30)
[Cosalen]ClO_4	1,10-1,15	390 (3,15)
[Cusalen]	1,15-1,20	360 (3,31)
[Cosalen]	-	-

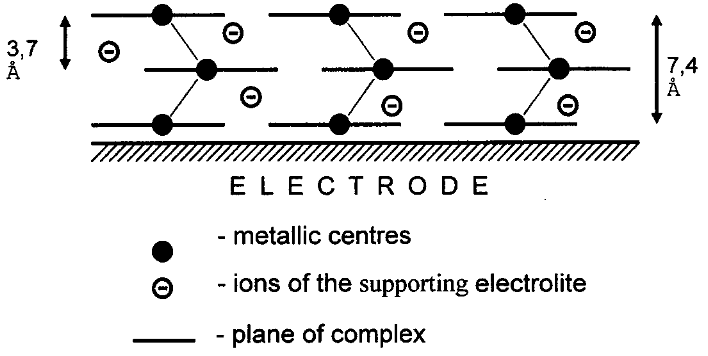

Fig.2: The model of structure of poly-[Pdsalen]

The overall transport rate is measurable as a diffusion constant D_{ct}. The values of charge diffusion coefficient along the polymeric chain lies in range of 10^{-9}-10^{-12} cm^2/s depending on the polymer, supporting electrolyte, temperature and film thickness (Tab. 2). For the first time it was established that the efficiency of charge separation and transport under the action of the electric field increases exponentially with increase of the metallopolymer thickness (Fig. 2).

The value of the activation barrier for the bimolecular reaction of electron transfer in the solid polymeric matrix does not exceed 30 kJ/mol (Tab. 2).

Tab. 2. Physico-chemical parameters of polymers

Polymer film	$D_{ct}\times10^{-10}$, cm^2·s^{-1}		$E_a\pm3$, kJ·mol^{-1}	λ_{max}, nm	ΔE(hν), mV reduced form
	0,6	1,5			
	μm				
poly-*[Pdsalen]*	2,0	5,0	30	800	450
poly-*[Pdsalphen]*	1,8	3,8	20	810	300
poly-*[Pdsalpn-1,2]*	1,1	5,6	-	760	340
poly-*[Pdsalpn-1,3]*	1,0	7,2	-	750	290
poly-*[Cusalen]*	0,3	0,6	27	680	350
poly-*[Cusalphen]*	0,5	0,9	25	780	280
poly-*[Nisalen]*	2,8	15	-	-	120
poly-*[Nisalphen]*	2,9	18	-	-	-
poly-*[Cosalen]*	1,3	2,6	-	680	100
poly-*[Ptsalphen]*	1,1	1,8	-	680	350
poly-*[Ptsalen]*	0,8	1,6	-	660	360
poly-*[Ptsalpn-1,2]*	0,7	1,4	-	660	290
poly-*[Ptsalpn-1,3]*	0,9	2,3	-	660	330

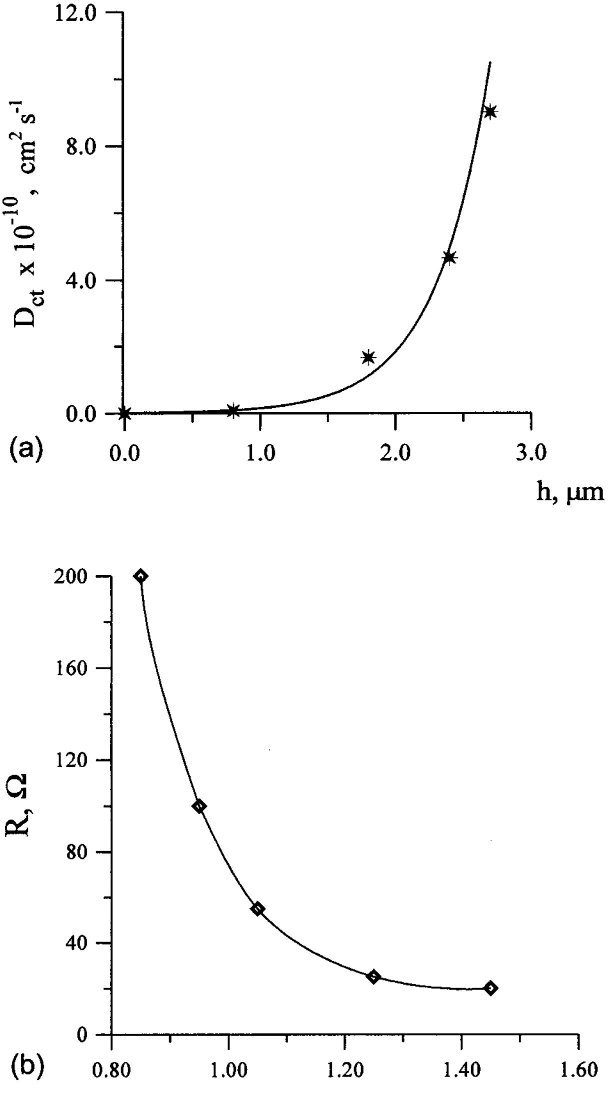

Fig. 3: The magnitudes of the charge transfer diffusion coeffitient (D_{ct}) (a) and ohmic resistance (R) (b) *[Pdsalen]*-based films depending the polymer thickness.

Using a microsonding installation, the pronounced anisotropy of the electrical properties of the polymeric films was determined. The ohmic resistance of the thin films in the direction parallel and perpendicular to the microelectrode surface of gold-coated α-Al_2O_3 differs as 1 : 10^6-10^9 depending on the polymers and experimental conditions$^{4)}$.

Electrochemical calculation, direct measurement of film thickness by the interferometry method and data of conduction anisotropy provided a basis for the refinement of the electrochemical notion of physical thickness of multimolecular layer films. These results also allowed to support our hypothesis of the formation mechanism of "molecular wires".

The crystalline structure of both oxidized and reduced forms of poly-[Msalen], where M ≡ Pd, Cu, was established$^{4)}$. It was shown that the degree of order of the monomeric sites is much higher in the case of the oxidized polymeric form. The crystalline structure of the film based on [Pdsalen] comprises alternating regular monolayers parallel to the electrode surface with an identity period 7,4 Å and a layer distance of 3,7 Å (Fig. 3).

The high photoactivity of polymers was discovered. The photopotential for the heterotriadic systems ran up to the values of 100-450 mV depending on polymers, thickness polymers, conditions of experiments (Tab. 2). A qualitative model for the processes of light energy accumulation was proposed.

By the spectral-luminescence method it was discovered that the complexes Pt(II) with salen, salpn-1,2 and salpn-1,3 aggregate$^{5)}$. On the basis of obtained data stable supramolecular assemblies were predicted and synthesized by electrochemical method. New polymers based on the complex compounds of platinum (II) possess emission properties.

Conclusion

It was shown that it is possible to create a new generation of "molecular rods" functioning under the action of electrical field and UV and visible light.

Stable polymers with one-dimensional, reversible, controlled photo- and electroinduced charge transfer in solid polymeric matrix may be used for the creation of photosensitizers, photo- and electrocatalysts, and temperature sensors.

Acknowledgments

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