



Molecular scale organized polyconjugated polymer–heteropolyacid composites

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Abstract. Hybrid organic–inorganic molecular-organized materials based on a conductive polymer – poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylenevinylene] (MDMO-PPV) – doped with Keggin-type heteropolyacids (polyoxometalates) were synthesized. It is shown that the rate of chemical interaction between MDMO-PPV and heteropolyacids correlates with the oxidative activity and acidity of the latter and leads to the formation of tertiary structures due to a strong electrostatic interaction of each 4–6 monomer units of the polymer with the heteropolyacid anion cluster. This interaction manifests itself in the appearance of an intensive EPR signal characteristic of the unpaired electron localized in the conjugated polymer matrix as well as in the changes in optical, photoelectrochemical, and photoluminescence properties of the composite films.

Key words: polymer materials, polyconjugated polymer, poly(phenylenevinylene), polyoxometalates, heteropolyacids, bulk heterojunction, nanocomposites.

INTRODUCTION

Hybrid organic–inorganic molecular-organized materials based on polyconjugated conducting polymers and inorganic nanoparticles are of great interest for developing new types of plastic solar cells and light emitting diodes, electrochemical sensors, and catalytic and electrocatalytic systems [1–5]. For the creation of these materials nanosized particles of CdS, CdSe, TiO₂, CuInS₂, PbS, fullerenes, and other electron acceptor species possessing semiconductor properties have been embedded into poly-*p*-phenylenevinylene, polythiophene, polyaniline, and polypyrrole matrixes [6–9].

The aim of the present work was to extend the range of such organic–inorganic heterostructures by fabricating composites based on a conjugated polymer – poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylenevinylene] (MDMO-PPV) – mixed with inorganic electron acceptors – Keggin-type polyoxometalates in the form of heteropolyacids (H₃PMo₁₂O₄₀, H₃PMo₁₁VO₄₀,

H₄SiMo₁₂O₄₀, H₃PW₁₂O₄₀, H₄SiW₁₂O₄₀) and their neutral salts (e. g. [(C₄H₉)₄N]₃PMo₁₂O₄₀).

Polyoxometalates comprise a unique family of metal–oxygen clusters that contain a well-defined number of atoms; they are from ca. 1 to 3–4 nm in size and in semiconductor terminology they may be considered as practically ideal quantum size clusters (quantum dots) [5,10,11]. Their semiconductor, redox, and photochemical properties are analogous to those of related oxides, such as WO₃ and MoO₃, and in many cases these properties of polyoxometalates are more pronounced than those of corresponding oxide nanoparticles [10].

EXPERIMENTAL

Solutions of MDMO-PPV in a concentration of 0.01 mol/L calculated for the monomeric unit and 0.04 mol/L solutions of the heteropolyacid in a methanol–chloroform mixture (1:1, by volume) were used for the investigation of the interaction between the

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polymer and the heteropolyacid. MDMO-PPV films with a thickness of about 10 μm were deposited onto quartz supports (for optical measurements) and onto optically transparent conductive SnO_2 electrodes (for electrochemical investigations) from 5% polymer solution in chlorobenzene.

Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E-3 X-band spectrometer at 77 K and at room temperature. The standards for the calculation of g -factor values were a 2,2-diphenyl-1-picrylhydrazyl sample ($g = 2.0036$) and Mn^{2+} ions in MgO matrix. The content of paramagnetic centres in the samples was measured by double integration of the spectra using subsequent comparison with a $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ single crystal standard having a known number of spins.

Photoluminescence (PL) spectra were recorded with a Spex Fluorolog-3 spectrofluorometer and optical absorbance spectra with a Specord M-40 spectrophotometer. Electrochemical measurements were conducted with the use of a PI-50-1 potentiostat, a PR-8 programmer, and a standard three-electrode cell equipped with a saturated Ag/AgCl reference electrode and a Pt counter electrode.

Electro- and photoelectrochemical measurements were performed with a PI-50-1 potentiostat and a PR-8 programmer; a quartz three-electrode cell was equipped with a saturated Ag/AgCl reference electrode and a Pt counter electrode. As a light source a 1 kW xenon arc lamp with a double-grating monochromator was used.

RESULTS AND DISCUSSION

The interaction between the solution of the polymer in chloroform and the methanolic solution of heteropolyacids results in the formation of black lustrous deposits insoluble in water and organic solvents. The fastest reaction was observed in the case of phosphomolybdenum derivatives; it proceeded practically instantly. In general, the rate of interaction decreased in the order $\text{H}_3\text{PMo}_{12}\text{O}_{40} > \text{H}_4\text{SiMo}_{12}\text{O}_{40} \gg \text{H}_3\text{PW}_{12}\text{O}_{40} > \text{H}_4\text{SiW}_{12}\text{O}_{40} \gg [(\text{C}_4\text{H}_9)_4\text{N}]_3\text{PMo}_{12}\text{O}_{40}$, and correlated appreciably with the oxidative activity and acidity of heteropolyacids.

The most complete interaction between MDMO-PPV and heteropolyacid took place in the case of a molar ratio of the compounds equal to one mole of heteropolyacid per 4–5 moles of the monomer units of the polymeric chain. It should be pointed out that this stoichiometry is in a good agreement with the results of the chemical analysis of the obtained deposit. Its annealing in the air at 900 °C for 30 min gave a solid (21% by weight), which consisted of pure MoO_3 units corresponding to one heteropolyacid molecule per four monomer units of the polymer chain. On the other hand,

the chemical elemental analysis of the organic moiety of the MDMO-PPV–heteropolyacid deposits indicated that MDMO-PPV did not undergo essential chemical transformations in its interaction with polyoxometalates, because the percentages of carbon (78.8%), hydrogen (9.7%), and oxygen (11.5%) in the organic moieties of the composite remained practically the same as in the untreated MDMO-PPV (79.1%, 9.8%, and 11.1%, correspondingly). However, other properties of the polymer – colour, solubility, etc. – dramatically changed.

The changes in the polymer matrix are additionally illustrated by the data obtained by EPR spectroscopy. It is well known that neither MDMO-PPV nor phosphomolibdic heteropolyacids show an EPR signal at room or low (77 K) temperatures. Contrary to this, MDMO-PPV–heteropolyacid composites exhibit EPR signals (Fig. 1) corresponding to two types of paramagnetic centres. An intensive narrow single line with a g -factor of 2.0025 and a line width ΔH of 1.1 G is characteristic of an unpaired electron localized in a conjugated polymer matrix. The second broad ($\Delta H = 20$ G) signal at a higher magnetic field can be attributed to Mo^{5+} ions; its g -value of 1.955 is in a good agreement with literature data ($g = 1.951$) [12].

Variations in the molar ratio of starting components in the range of 0.02 to 1.0 practically did not influence the line width. This fact allows us to conclude that there is no dipole–dipole interaction between stabilized electrons and Mo^{5+} centres in the heteropolyacid anion, which means that the distance between the neighbouring paramagnetic centres is larger than 2.5–3 nm. In the case of MDMO-PPV doped with $\text{H}_3\text{PVMo}_{11}\text{O}_{40}$ (Fig. 2, curve 2), vanadium-substituted phosphomolibdinum anions reveal a strong EPR signal characteristic of V^{4+} ions, which originally exist in the heteropolyacid molecule. The introduction of these vanadium-containing clusters led to a substantial increase in the width of

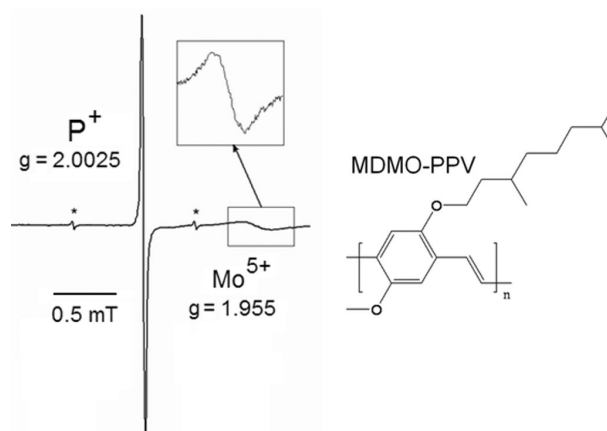


Fig. 1. Typical EPR spectra of the MDMO-PPV–heteropolyacid composite at 77 K.

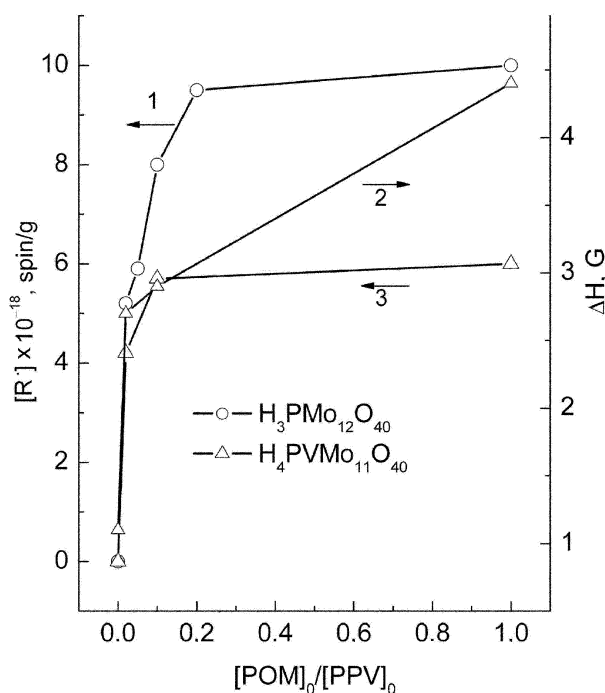


Fig. 2. Dependence of stabilized unpaired electron concentrations $[R\cdot]$ and EPR line width (ΔH) for MDMO-PPV treated with $H_3PMo_{12}O_{40}$ (1) and $H_3PVMo_{11}O_{40}$ (2,3) on the ratio of the initial molar concentrations of heteropolyacids, $[POM]_0$, and polymer (calculated on a monomer unit), $[PPV]_0$.

the line attributed to paramagnetic centres of MDMO-PPV, which reflects the existence of a rather weak magnetic dipole–dipole coupling between the unpaired electrons of the polymer cation radicals and V^{4+} centres. In accordance with this dipole broadening, a calculation of the average distance between the neighbouring radicals and V^{4+} centres in the composite showed that the distance between spins was not less than 1.8–2.0 nm.

Figure 2 shows the dependence of the concentration of stabilized unpaired electrons in MDMO-PPV on the molar ratio of heteropolyacids and MDMO-PPV (calculated for the monomer unit of the polymer) used in the synthesis of the composites. As can be seen from the plot, the concentration of paramagnetic centres grows with increasing content of polyoxometalate in the reaction mixtures only up to a MDMO-PPV-to-polyoxometalate ratio of approximately (4–5) : 1.

As indicated above, this ratio of the components is in close agreement with the data of the chemical analysis of MDMO-PPV–polyoxometalate composites prepared at a 1 : 1 ratio of the starting components. In these conditions, if the content of polyoxometalate in the reaction mixture is higher than one molecule per four to six monomer units of the polymer, excess polyoxometalate molecules will not react with the polymer and thus will not cause a further increase of the concentration of paramagnetic centres. Hence, the EPR

data, along with the results of chemical analysis, indicate a distinct relation between the content of heteropolyacid and polymeric components in the composites.

To summarize, the interaction between MDMO-PPV and heteropolyacids is characterized by a distinct stoichiometry; it does not influence the chemical formulation of the polymer but it leads to a sharp decrease in solubility and to the appearance of unpaired electrons. Based on these facts we can suggest that the main result of this interaction is the formation of a charge-transfer complex between heteropolyacid anion clusters and conformationally distorted polymer chains.

For the investigation of optical, photoluminescence, and photoelectrochemical properties of a charge-transfer complex thin polymer films deposited onto optically transparent quartz substrates were employed. The rate of the interaction between MDMO-PPV films and heteropolyacids as well as the depth of film transformation crucially depended on the solvent used. After the treatment of MDMO-PPV films with methanolic solutions of heteropolyacids no visible changes of the polymer were observed. Evidently it is connected with the insolubility of MDMO-PPV in methanol; hence heteropolyacid clusters could penetrate the MDMO-PPV film only to a depth close to the monomolecular surface layer.

Contrary to this, if the solution of the heteropolyacid in the chloroform–methanol mixture was used, the treated films lost their red colour and became dark grey. In this case heteropolyacid clusters could penetrate into the bulk of the polymer, and a bulk heterostructure was formed.

This process manifested itself in pronounced differences in the optical absorbance spectra of MDMO-PPV films before and after their treatment with the solution of heteropolyacid in the chloroform–methanol mixture. As Fig. 3a shows, the main peak of MDMO-PPV absorption sharply decreases, and a new wide long-wavelength peak appears at approximately 700–800 nm. In the case of heteropolyacids dissolved in the chloroform–methanol mixture, 1 : 2, these spectral transformations were usually completed in several minutes for $H_3PMo_{12}O_{40}$ and in 14–16 h in the case of $H_3PW_{12}O_{40}$.

Figure 3b illustrates an enhancement of the long-wavelength absorbance and, simultaneously, a reduction of the main peak of the MDMO-PPV absorbance as a function of increasing chloroform content in the heteropolyacid solution used for treating the polymer. Evidently, in this case the depth of the penetration of heteropolyacid acids into the bulk of the polymer was a determining factor for completing the transformation of the polymer to the polymer–heteropolyacids composite.

The formation of the bulk heterostructure led to significant changes in the photoluminescence spectra (Fig. 4a). In these spectra there was no peak at 593 nm

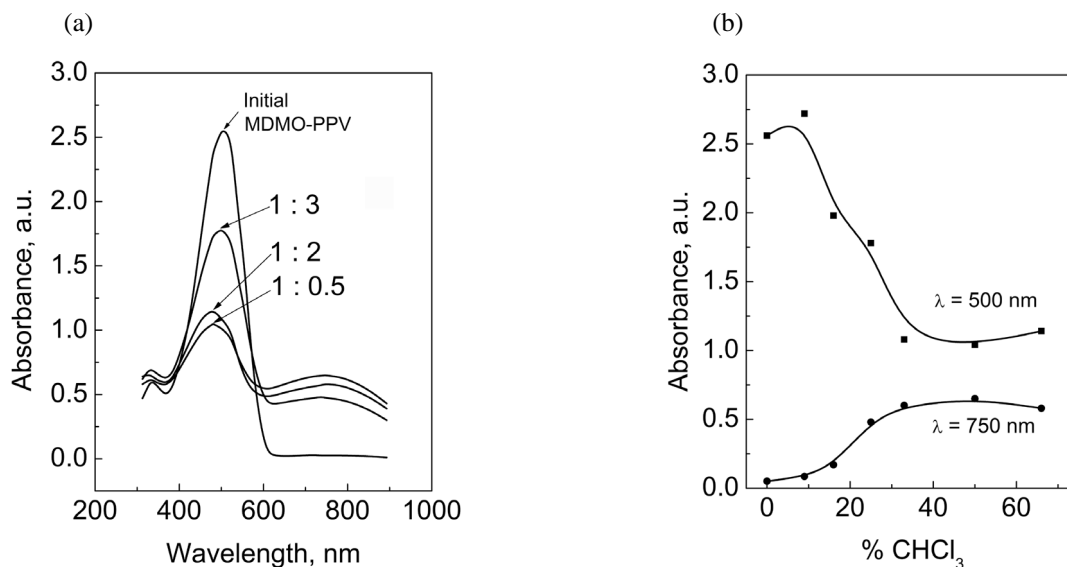


Fig. 3. Optical absorbance spectra of MDMO-PPV films before and after their treatment with $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ solutions with various methanol-to-chloroform molar ratios (a); dependence of the absorbance of MDMO-PPV films treated with $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ solutions at long- and short-wavelength peaks (750 and 500 nm, correspondingly) on the chloroform content in methanol–chloroform mixtures (b).

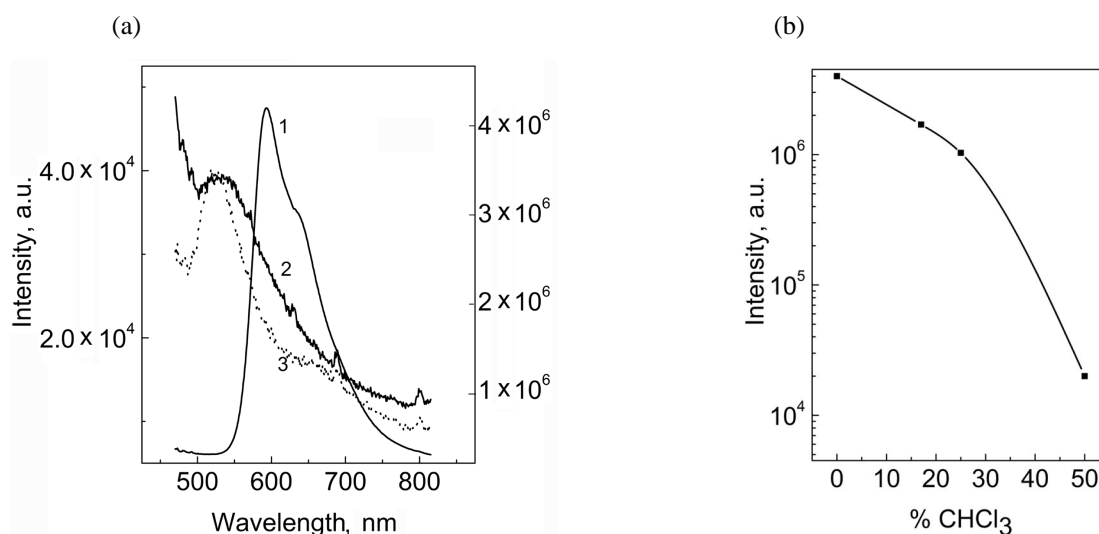


Fig. 4. Photoluminescence spectra (a) of a MDMO-PPV film as deposited (1) and after the treatment with $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ dissolved in a methanol–chloroform mixture, 1 : 1 (2) and 2 : 1 (3); the intensity of photoluminescence of MDMO-PPV films treated with $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ solutions in a methanol–chloroform mixture as a function of chloroform content (b). The wavelength of excitation is 420 nm.

with a shoulder at 640 nm characteristic of MDMO-PPV, instead a new short-wavelength peak at 525 nm appeared. The treatment of PPV film with $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ dissolved in the methanol–chloroform mixture led to an intensity of luminescence decreased by two orders of magnitude with increasing chloroform content (Fig. 4b).

Similar spectral behaviour was also observed in the case of MDMO-PPV films treated with tungsten phosphate and other polyoxometalates in the form of heteropolyacids.

These changes are due to the transformations in the conjugated polymer chain, which can also influence the

charge-transfer processes. We investigated this effect with electrochemical techniques using PPV films deposited onto optically transparent quartz substrates covered with an ITO (indium-tin oxide) layer. Comparison of cyclic voltammograms of MDMO-PPV film electrodes registered in 0.1 M $(C_4H_9)_4NBF_4$ acetonitrile electrolyte reveals that both anodic and cathodic currents markedly grow after the treatment of the polymer with the heteropolyacid solutions in a methanol–chloroform mixture [3]. On the other hand, after passing a cathodic charge through the composite MDMO-PPV–polyoxometalate film, the bluish-grey colour of the composite film turned red, characteristic of pure MDMO-PPV. Then, after passing an anodic charge at potentials higher than +1 V, the red colour of the polymer film transformed again to the bluish-grey characteristic of the MDMO-PPV–heteropolyacid composite. The change in colour of the composite film from bluish-grey to red is attributed to an electron injection from the ITO conduction band into the composite, which led to cathodic reduction of Mo(VI) to Mo(V) and, as a result, to disrupting the charge transfer complex. The anodic polarization, in turn, caused the oxidation of Mo(V) to Mo(VI), accompanied by a proton injection from the electrolyte to the composite film, which led back to the formation of a charge transfer complex involving heteropolyanions and polymer molecule. Such reversibility may serve as another substantial argument in favour of the fact that the interaction of PPV with polyoxometalates does not lead to destructive chemical transformations of the polymer in

spite of strong alterations in its chromophore (poly-conjugated) system.

An enhancement of the electrocatalytic activity of the polymer due to bulk heterojunction and charge-transfer complex formation allows improvement of the functional characteristics of photoelectrochemical cells based on the use of MDMO-PPV as a semiconductive photosensitive element. As is seen from Fig. 5a, the treatment of a MDMO-PPV film with a heteropolyacid solution enhances the values of photocurrent to be measured in the photoelectrochemical cell. We connect this increase in photoresponse with a strongly enhanced electrocatalytic activity of the modified surface and, consequently, with a decreased overvoltage at the polymer–electrolyte interface. Additionally, in the photovoltage spectrum (Fig. 5b) one can observe the appearance of a long-wavelength photoresponse attributed to a photogeneration process involving the charge-transfer complex. Moreover, the long-term stability of hybrid electrodes increases markedly (2–5 times) due to the formation of a thin surface layer consisting of the products of the polymer–heteropolyacid interaction. As a result, it becomes possible to perform long-term electro- and photoelectrochemical experiments even in the presence of strong donor and acceptor additives in the electrolyte. Evidently such protective treatment could be useful for various applications – electrochemical sensors, electrocatalytic and other systems in which the polymer is in contact with reactive media.

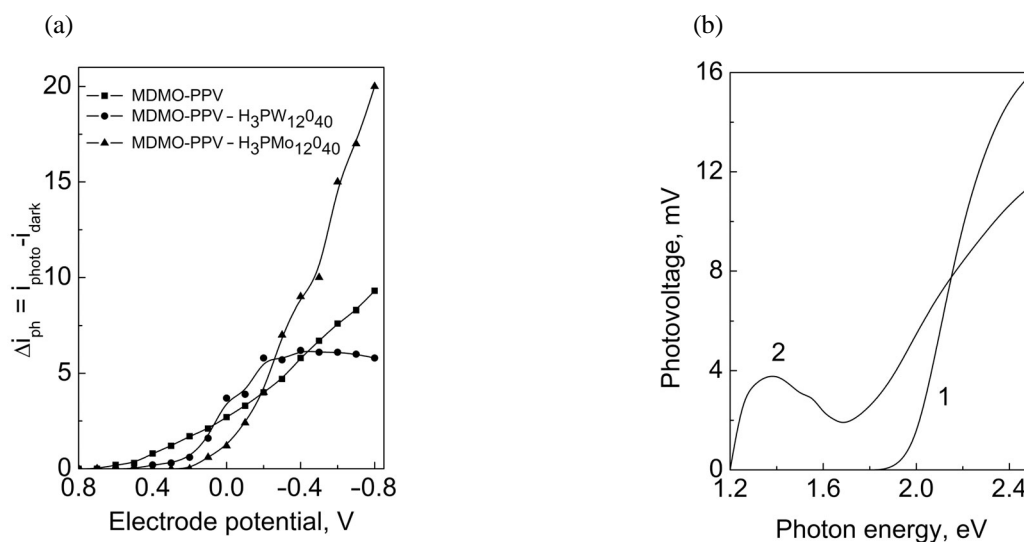


Fig. 5. Photocurrent-voltage dependence of MDMO-PPV film as deposited and after the treatment with heteropolyacid solutions (a); photovoltage spectra of MDMO-PPV film as deposited (1) and after the treatment with $H_3PMo_{12}O_{40}$ (2) (b).

CONCLUSIONS

Based on the experimental data obtained with the use of optical absorbance and luminescence spectroscopy as well as on the results of electrochemical and EPR measurements and the data of chemical analysis, we can conclude that the interaction of MDMO-PPV with heteropolyacids leads to the formation of strong charge-transfer complexes. This interaction does not cause irreversible destructive transformations in the polymer chain. The introduction of polyoxometalate clusters into a PPV matrix is not equivalent to classical acid doping well known for polyaniline–heteropolyacid systems but it causes reversible alterations in the polymer electronic structure, which lead to substantial changes in the optical, photoluminescence, and photoelectrochemical spectra, as well as to an increase of free charge carrier concentrations and to an enhancement of the electrocatalytic activity of the polymer surface. A novel hybrid material obtained in the framework of this work may be prominent as an active component of photoelectrochemical cells and other electro- and photoelectrochemical devices.

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Molekulaartasemel struktureeritud polükonjugeeritud polümeer-heteropolühapete komposiidid

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On sünteesitud keegintüübiliste heteropolühapetega (polüoksometalaadid) dopeeritud juhtival polü[2-metoksü-5-(3',7'-dimetüülloktüülloksü)-*p*-fenüleenvinüleenil] (MDMO-PPV) põhinevad molekulaartasemel struktureeritud orgaanilised-anorgaanilised hübriidmaterjalid. On näidatud, et MDMO-PPV ja heteropolühapete vahelise keemilise koostoime ulatus on korrelatsioonis heteropolühapete oksüdeerimisomaduste tugevuse ning happelisusega ja see põhjustab polümeeri iga 4–6 monomeerühiku tugeva elektrostaatilise vastasmõju tõttu tertsiarsete heteropolühapete anioondomeenide moodustumise. Selline koostoime väljendub intensiivse EPR-signaalina, mis on omane konjugeeritud polümeermaatriksis paiknevale paardumata elektronile, samuti ka muutustena komposiitkile optilistes, fotoelektrokeemilistes ja fotoluminestsentsi omadustes.