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**Summary of the Ph.D. Thesis**  
Autoreferát disertační práce



**Novel conjugated polymers of the metallo-supramolecular and  
polyelectrolyte class**

Nové konjugované polymery metalo-supramolekulárního a  
polyelektrolytového typu

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## **Abstract**

This thesis targets the development of conjugated polymers with improved process ability from solutions. Two types of ionic polymers are addressed: (i) conjugated metallo-supramolecular polymers (MSPs) composed of conjugated heteroaromatic unimers (building blocks) linked to chains by various metal ions giving charged main chains, and (ii) polythiophene polyelectrolytes containing ionic pendants. Processing advantages of conjugated polyelectrolytes consist in the possibility of their processing from solutions in green solvents such as alcohols or even water. The advantages of MSPs consist in the thermodynamic control of the degree of polymerization (length) of their chains in solutions by the choice of solvent and temperature. As a result, MSPs reversibly provide systems of low viscosity that can be processed from solutions more easily than high-molar-mass polymers giving highly viscous solutions.

Synthesis of appropriately designed unimer(s) is the key step of preparation of an MSP. Within this thesis, a series of novel unimers composed of linear oligothiophene type (mono-, bi-, ter- a thieno-thiophene- diyl) central blocks capped with 2,6-bis(oxazoline-2-yl)pyridine (*pybox*) or 2,6-bis(imidazole-2-yl)pyridine (*bzimpy*) end-groups have been successfully prepared, characterized and assembled with various metal ions into MSPs. It is worth noting that the cheap and commercially easy available chelidamic acid was the starting compound for the syntheses of both the above chelating end-groups (ion selectors).

The bis(*pybox*) unimers were assembled with metal ions such as  $\text{Fe}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and lanthanide ions  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  to give corresponding MSPs. On the other hand, MSPs derived from bis(*bzimpy*) unimers were found to show significantly lower solubility thus they were studied less in detailed using only  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$  ion couplers. The detailed study of the MSP assembly revealed three stages of this process, same as observed for bis(*tpy*) unimers: formation of “butterfly” dimers  $\text{U-Mt}^{z+}\text{-U}$  (U stands for a unimer species) at the  $\text{Mt}^{z+}/\text{U}$  mole ratios  $r$  up to ca 0.5, formation of longer MSP chains for  $r$  from above 0.5 to ca 1, and end-capping of MSP chains and their equilibrium depolymerization at  $r$  values above 1. The latter proves the constitutional-dynamic nature of the novel MSPs, which is the fastest for Zn-dynamers and the slowest for Fe-dynamers that exhibit the presence of the metal-to-ligand charge transfer transitions. Photoluminescence properties of new *pybox*- and *bzimpy*-MSPs are

also similar to those of the *tpy*-MSPs; only  $Zn^{2+}$ -MSPs show high photoluminescence while the other ones exhibit quenching the luminescence with increasing content of metal ions.

Novel cationic conjugated polyelectrolytes have been prepared by modification of the parent poly[3-(6-bromohexyl)thiophene-2,5-diyl bromide]s of the low to high regioregularity, consisting in replacing the bromine side-chain-capping atoms with triethyl- or triphenyl-phosphonium bromide groups. The parent polymers were prepared by means of the Grignard metathesis polymerization and their regioregularity has been tuned by temperature regime of the polymerization process. Studies on the optical properties of these polyelectrolytes revealed their solvatochromism and possibility of tuning their luminescence through the solvent polarity. The luminescence quenching by  $K_4[Fe(CN)_6]$  and  $K_3[Fe(CN)_6]$  has been also studied. All experiments performed point to the principle influence of the main-chain regioregularity on the polymer properties except for its solubility in polar solvents.

**Keywords:** conjugated polymer, constitutional dynamic polymer, dynamer, ionic polymer, luminescence quenching, polyelectrolyte, polythiophene, self-assembly.

## ***Introduction***

Conjugated polymers derived from heterocycles such as thiophene and pyrrole are widely studied as electroactive materials for applications in the field of organic and composed organic/inorganic electronic devices.<sup>1-4</sup> These materials are generally processed from solutions, which brings about demands for their properties enabling easy and ecologically friendly processing conditions. Such demands meet conjugated polymers that can tunably form appropriately viscous solutions of reasonably high concentrations and polymers that are soluble in environmentally friendly solvents such as alcohols or ideally water.

The demands of the first type can particularly meet newly emerged class of polymers – conjugated constitutional dynamic polymers referred to as dynamers. These polymers are composed of mostly oligomeric molecules that

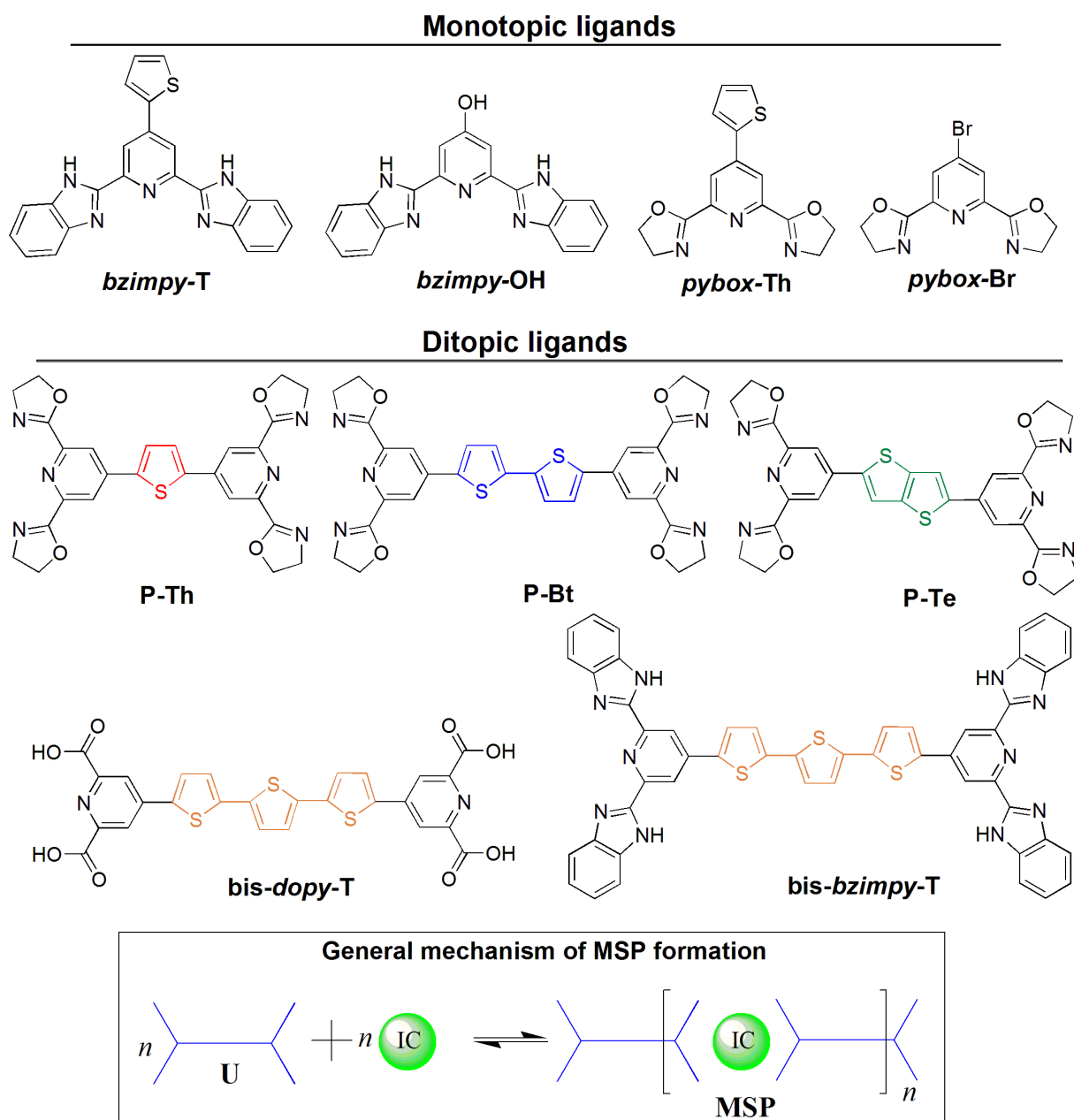
are linked to chains reversibly by linkages, the stability of which is controlled thermodynamically (not by activation energy). Such polymers can thus reversibly self-assemble or depolymerize in a suitable solution and/or at elevated temperature and thus be easily processed but it should become a high-molar-mass polymer in the solid state functional layer. The second type demands fulfilled conjugated polymers with ionic side groups, i.e., polymers of the polyelectrolyte class that are soluble in water-miscible solvents or even in water. Perhaps the ideal systems might be constitutional dynamic polymers with ionic side groups that meet both the above demands.<sup>5</sup>

This thesis deals with the preparation of novel polymers of both the above mentioned types. As conjugated dynamers were chosen those of the metallo-supramolecular type usually called metallo-supramolecular polymers (MSPs). MSPs are composed of conjugated, mostly oligo-heteroaromatic building blocks referred to as unimers, which are linked to chains by coordination binding of their chelate end-groups to various metal ions. Novelty of the materials prepared consists in usage of seldomly used chelate groups derived from cheap chelidamic acid as chelate end-groups of oligothiophene-based unimers. The second group of materials is represented by polythiophene polyelectrolytes containing pendants capped with phosphonium type groups.

### ***Aims of Thesis and Strategy of Solution***

General aim of my thesis was the development of novel conjugated polymers with improved processability from solutions. Two types of novel polymers have to be addressed within this project:

- conjugated metallo-supramolecular polymers (dynamers) derived from oligothiophenes capped with chelate end-groups derived from the benzimidazole and oxazoline derivatives of pyridine that can be prepared from cheap chelidamic acid, and
- polythiophene polyelectrolytes with phosphonium pendants that are soluble in aqueous mediums.



**Figure 1.** The ligands and unimers prepared and the scheme of the formation of MSPs; **U** stands for unimer and **IC** for ion coupler (metal ion).

The project solution required:

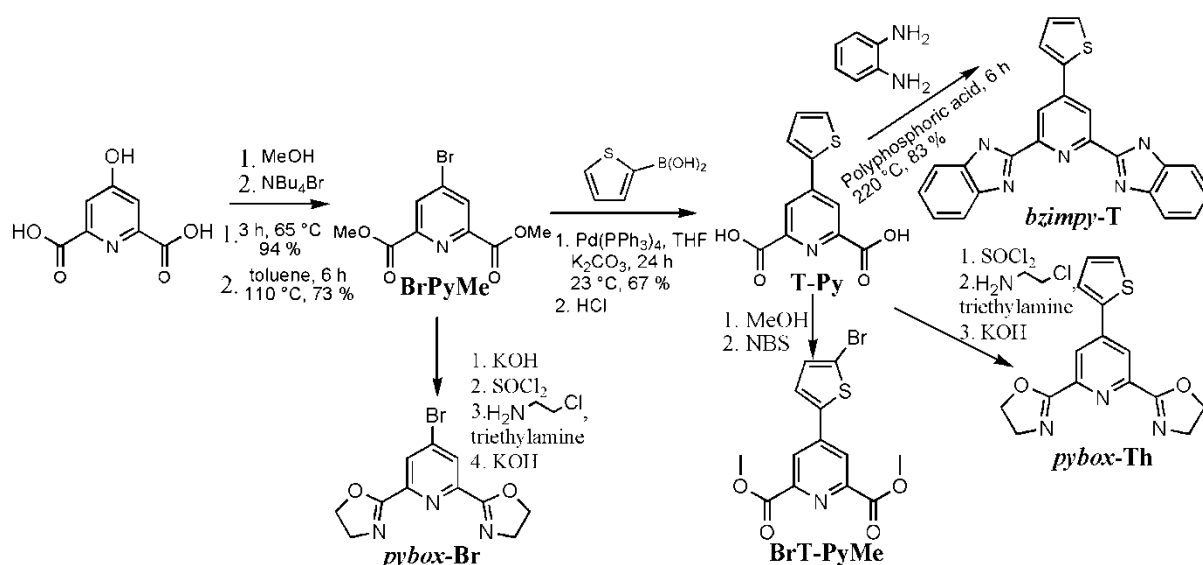
- Preparation of novel monotopic chelate ligands based on bis(benzimidazole)- and bis(oxazole)pyridyl moieties.
- Investigation of the complexation of synthesized ligands with metal ions and characterization of formed complexes in solution.

- Synthesis and characterization of conjugated ditopic unimers with the above chelate end-groups and oligothiophene central blocks.
- Preparation of metallo-supramolecular polymers by self-assembly process of synthesized unimers with metal ions. Analysis of prepared supramolecular assemblies by different spectroscopic methods.
- Detailed investigation of the process of self-assembling.
- Synthesis of precursor polymers: poly[3-(6-bromohexyl)thiophene]s of different regioregularity using the GRIM polymerization method.
- Transformation of the precursor polymers into cationic conjugated polyelectrolytes by their modification with trialkyl(aryl)phosphates and characterization of the prepared CPEs.

## Results and Discussion

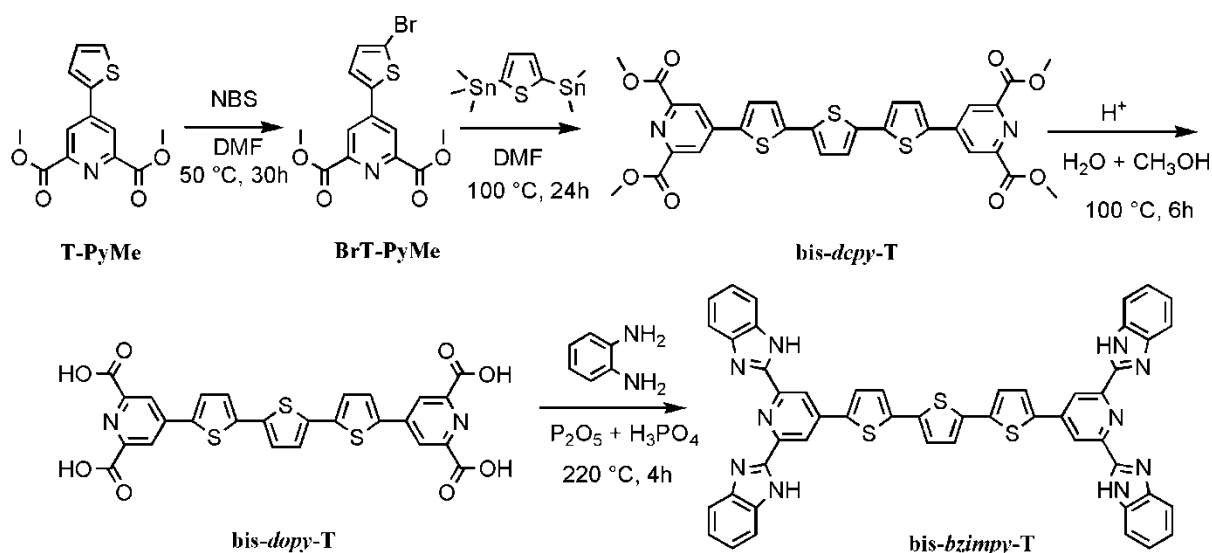
### Preparation of monotopic ligands and unimers

Preparation of monotopic benzimidazole ligands *bzimpy-OH*, *bzimpy-T* benzoxazole ligands *pybox-T*, *pybox-Br* started from cheap chelidamic acid using the reaction path shown in **Scheme 1**. The monotopic ligands were then exploited in the preparation of desired unimers (ditopic ligands, **Schemes 2 and 3**).



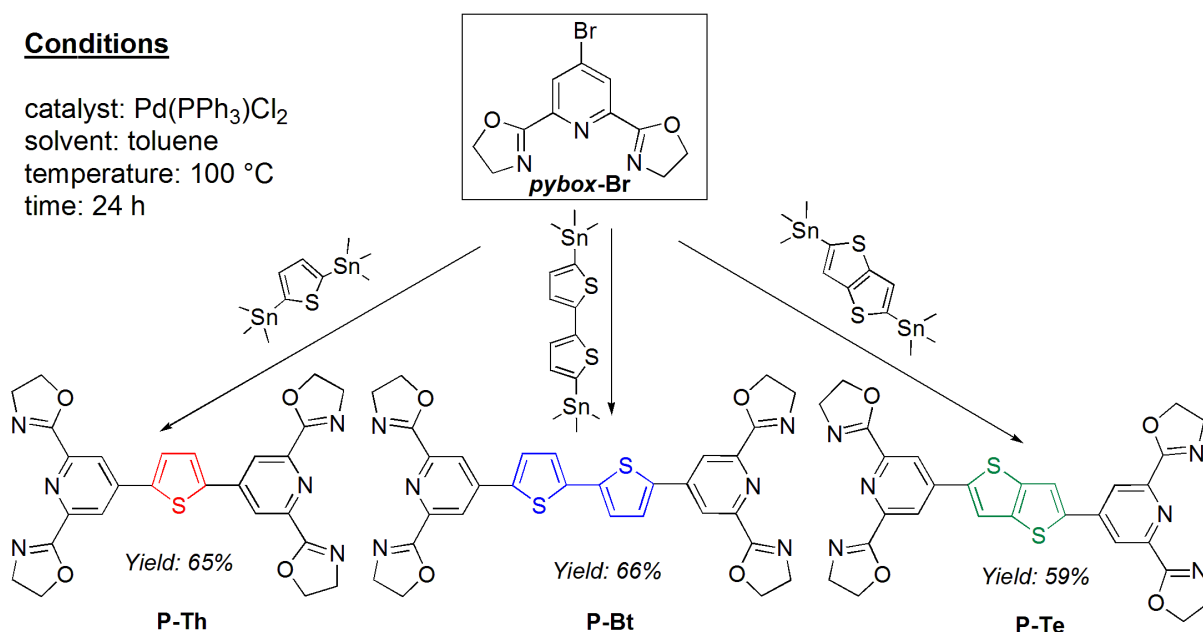
**Scheme 1.** Synthesis paths to monotopic ligands.

Benzimidazole based unimer **bis(bzimpy)T** was prepared by Stille coupling giving intermediate **bis(dcpy)T** unimer with ester groups that was then hydrolyzed to give tetracarboxy unimer subject to cyclization reaction with benzene-1,2-diamine in the presence of polyphosphoric acid. Bis(**dopy**) unimers were prepared by Stille coupling of activated **dopy** group precursor with bis(Me<sub>3</sub>Sn) derivative of the central block.



### Conditions

catalyst: Pd(PPh<sub>3</sub>)Cl<sub>2</sub>  
 solvent: toluene  
 temperature: 100 °C  
 time: 24 h



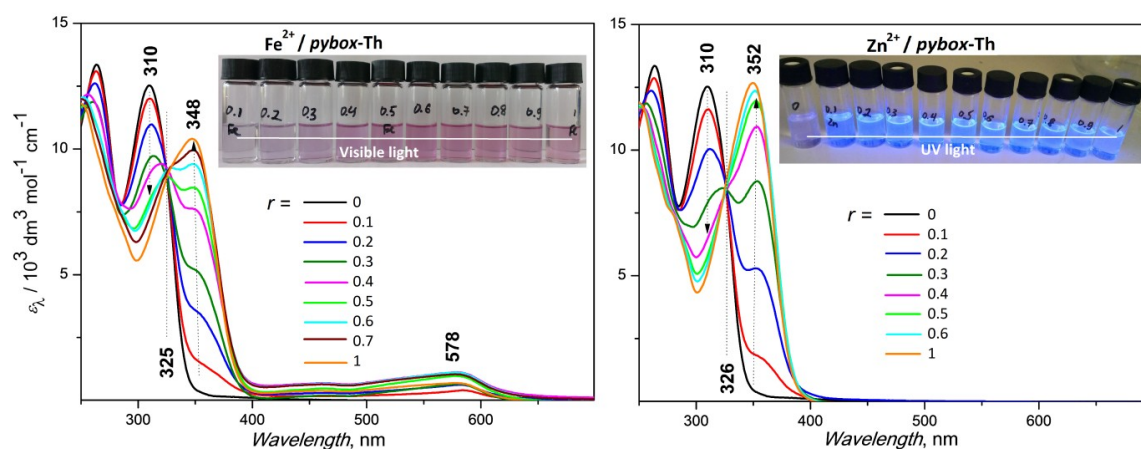
**Table 1.** Spectral data for **pybox** unimers; absorption maximum wavelength  $\lambda_A$  and molar absorption coefficient  $\varepsilon_{\max}$  ( $\text{m}^3 \text{mol}^{-1} \text{cm}^{-1}$ ); emission maximum wavelength  $\lambda_F$ ; Stokes shift  $\nu_s$ ; fluorescence quantum yield  $\phi_F$  (%).

	$\lambda_A$ , nm		$\varepsilon$	$\lambda_F$ , nm		$\nu_s$ , $\text{cm}^{-1}$		$\phi$ , %	
	sol.	film		sol.	film	sol.	film	sol.	film
<b>P-Th</b>	350	352	8.9	404	580	3 820	11 170	12.8	1.57
<b>P-Bt</b>	400	414	12.6	532	603	6 210	7 570	7.3	1.17
<b>P-Te</b>	373	381	15.3	510	554	7 210	8 200	14.3	1.45

### Complexation of monotopic ligands and unimers with metal ions

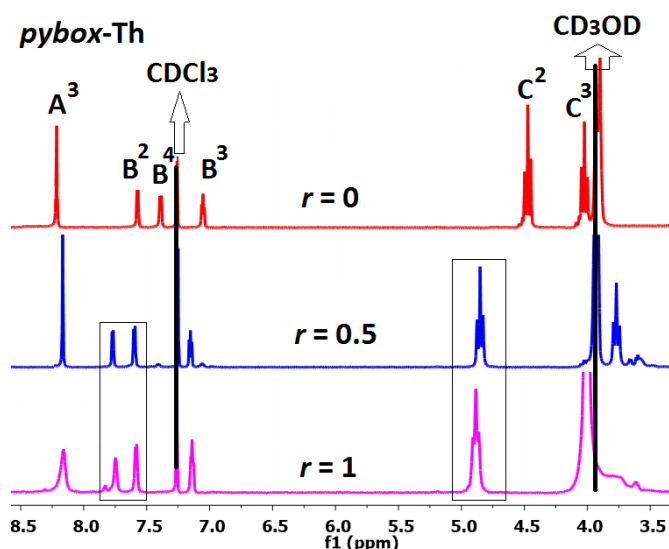
Complexation of monotopic ligands (L) with  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$  ions in dilute solutions was monitored by the UV/vis, luminescence and NMR spectroscopy using the constant ligand concentration and gradually increasing concentration of ions. The UV/vis spectra indicated a coincidence of presumed isosbestic points belonging to two consecutive transformations, similarly as observed for some complexes and MSPs derived from bis(*tpy*) unimers.<sup>6, 5</sup> Another explanation that **pybox** moieties does not form “butterfly dimers”  $\text{L-Mt}^{2+}\text{-L}$  but directly only species  $[\text{MtL}]^{2+}$  has been disproved by the NMR experiments that showed the two-step assembly according to the reactions:

- (i)  $\text{Mt}^{2+} + 2\text{L} \rightarrow [\text{MtL}_2]^{2+}$  at  $r \leq 0.5$ , and  
(ii)  $[\text{MtL}_2]^{2+} + \text{Mt}^{2+} \rightarrow 2 [\text{MtL}]^{2+}$  at  $r$  above 0.5.



**Figure 2.** UV/vis spectra of the  $\text{Fe}^{2+}$  and  $\text{Zn}^{2+}$  / **pybox-Th** systems of different composition ratio  $r = [\text{Mt}^{2+}] / [\text{U}]$ .



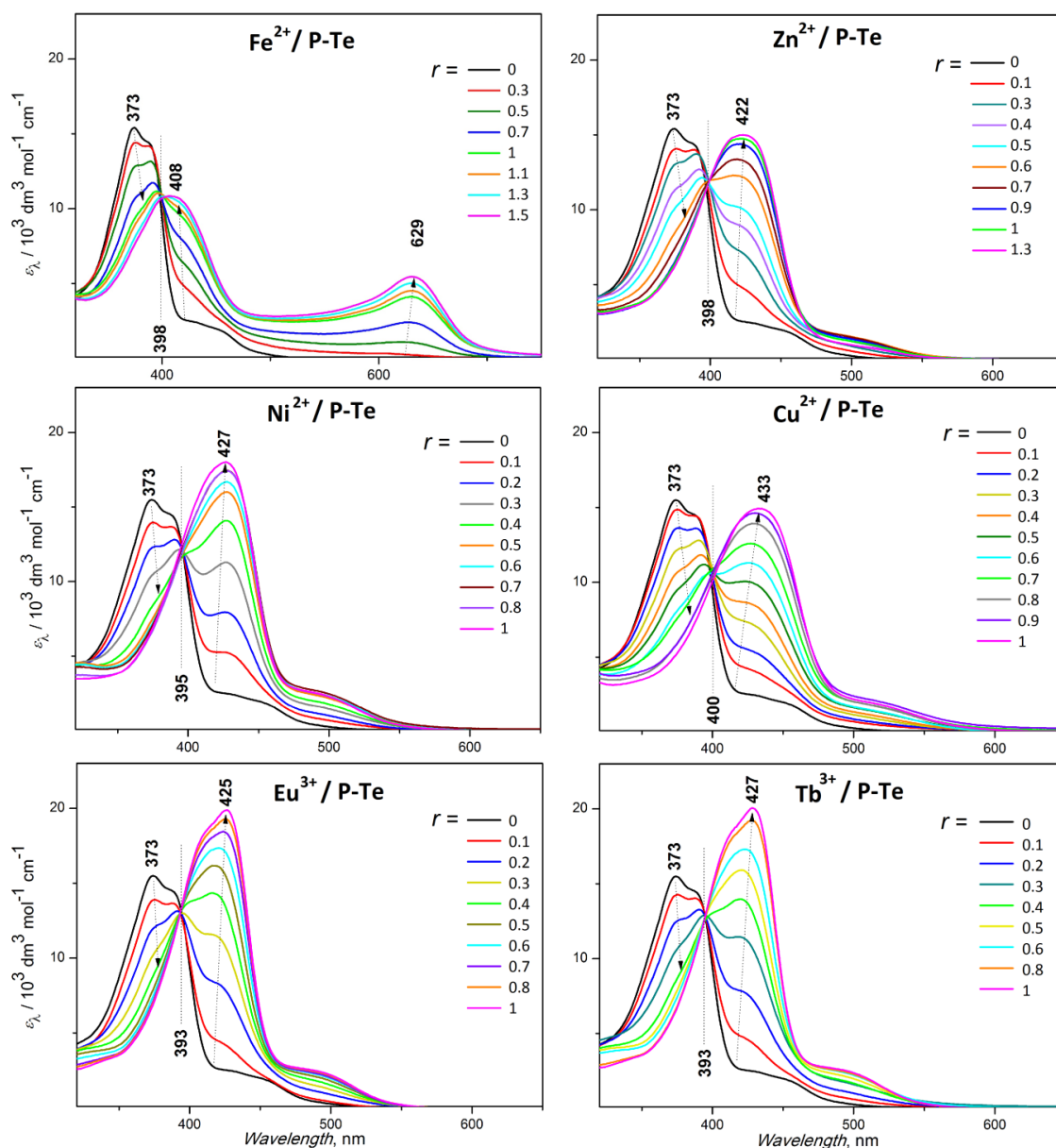


**Figure 3.**  $^1\text{H}$  NMR data for *pybox-Th* and its complexes with  $\text{Zn}^{2+}$  ions.

NMR spectra of the  $r = 0.5$  systems shows the signal of  $\text{C}^3$  protons shifted to lower fields (from 4.01 to 4.85 ppm) due to the decreased electron density in coordinated oxazole rings. On the contrary, the signal of  $\text{C}^2$  protons is shifted to higher fields (from 4.46 to 3.77 ppm) due to mutual shielding of  $\text{C}^2\text{-H}$  bonds belonging to two different ligands bound perpendicularly to the same  $\text{Zn}^{2+}$  ion (octahedral geometry). The spectrum of the  $r = 1$  system showed unchanged position of the  $\text{C}^3$  signal and almost absence of the signal at 3.77 ppm that is shifted to 4 ppm where overlaps with the solvent signal. Residual signals from 3.77 to 4 ppm indicate ongoing exchanges (constitutional dynamics) of the  $[\text{MtL}]^{2+}$  system according to reaction (ii).

*Self-assembly of unimers with  $\text{Mt}^{2+}$  ions* has been studied similarly as complexation of monotopic ligands. The UV/vis spectral changes caused by the gradual increase in the ratio  $r$  (**Fig. 4**) are characterized by attenuation of absorption bands of the free unimer and occurrence of new bands attributed to the formed MSPs oligomers (at low  $r$  values) and polymers (at higher  $r$  values). Crossings of the spectra indicating the presence of isosbestic points indicating the transformation of free unimer species into other well-defined species have been also observed. The assembling can be divided into three stages, same as assembling of bis(*tpy*)unimers described in literature:<sup>5</sup> (i) formation of butterfly dimers  $\text{U-Mt}^{2+}\text{-U}$  in systems with  $r < 0.5$ , (ii) growth of MSP chains  $[-\text{Mt}^{2+}\text{-U}]_n$  in systems with  $r$  from 0.5 to ca 1, and (iii) equilibrium dissociation of the longer MSP chains to shorter chains end capped with excess

Mt<sup>2+</sup> ions in systems with  $r > 1$ . The systems with Fe<sup>2+</sup> ion couplers have shown the MLCT band at relatively high positions from 629 to 635 nm, which are even higher than  $\lambda_{\text{MLCT}}$  determined for Fe-MSPs with central phosphole rings.<sup>7</sup>



**Figure 4.** UV/vis spectra of Mt<sup>2+</sup>/P-Te systems of various composition ratio  $r$ .

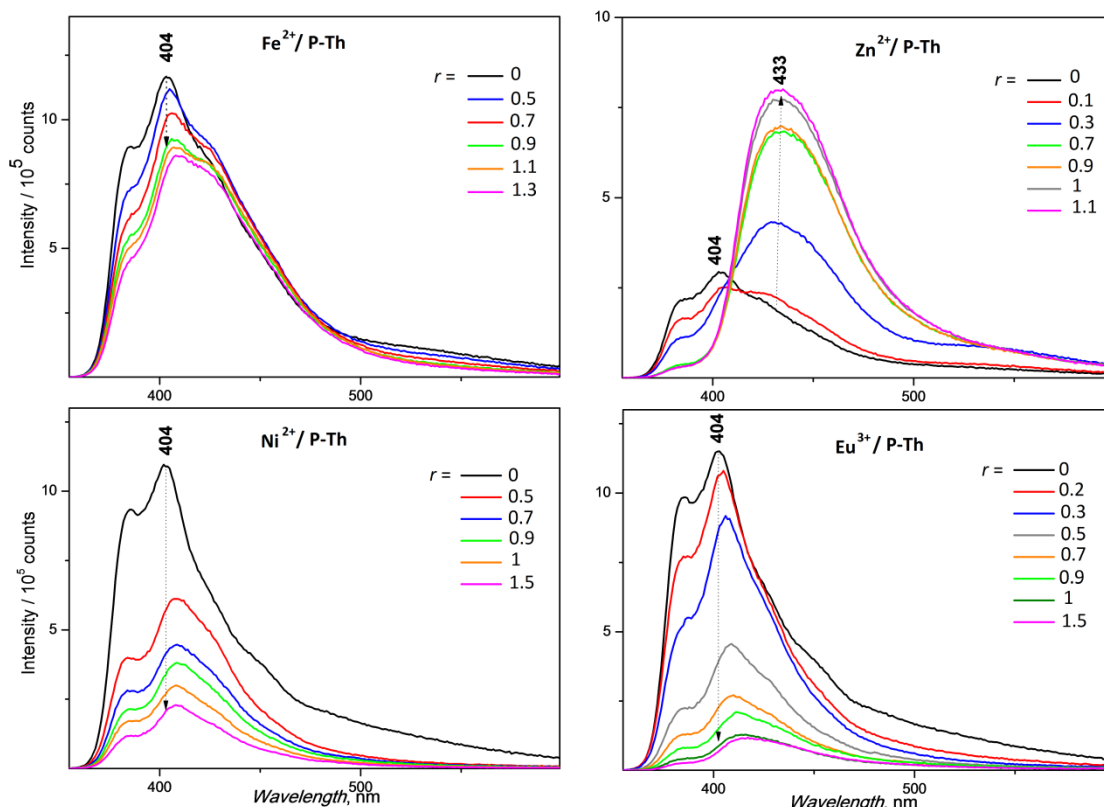
The positions of absorption maxima of formed MSPs strongly depend on the metal ion couplers used. The differences between absorption maxima position of unimers and their MSPs with various ions at  $r = 1$  are collected in **Table 2**. The highest red shifts when going from free unimer to its MSP were observed for Cu<sup>2+</sup>-MSPs, the lowest one for Fe<sup>2+</sup>-MSPs, which can be ascribed to partial transfer of the corresponding transitions to the MLCT band of these

MSPs, as observed for other systems.<sup>8, 7</sup> Examples of photoluminescence spectra of MSPs are shown in **Fig. 5**.

**Table 2.** Spectral data for solutions of **pybox** unimers (U) and MSPs ( $r = 1$ ):  $\lambda_A$ ,  $\lambda_e$  and  $\lambda_F$  are wavelengths of the absorption maximum, absorption edge and emission maximum, respectively,  $\epsilon_{\max}$  molar absorption coefficient for  $\lambda_A$  ( $\text{m}^3 \text{mol}^{-1} \text{cm}^{-1}$ );  $\nu_S$  Stokes shift ( $\text{cm}^{-1}$ ).

	U	Fe <sup>2+</sup> /U	Zn <sup>2+</sup> /U	Ni <sup>2+</sup> /U	Cu <sup>2+</sup> /U	Eu <sup>3+</sup> /U	Tb <sup>3+</sup> /U
<b>P-Th</b>							
$\lambda_A$ , nm	350	371	380	375	388	375	377
$\lambda_e$ , nm	491	698	516	523	538	505	509
$\epsilon_{\max}$	8.9	7.2	8.7	10.6	10.2	12.1	12.0
$\lambda_F$ , nm	404	408	434	409	421	415	421
$\nu_S$ , $\text{cm}^{-1}$	3820	2445	3270	2210	2020	2570	2770
<b>P-Bt</b>							
$\lambda_A$ , nm	400	411	445	449	457	439	443
$\lambda_e$ , nm	526	687	625	594	632	583	594
$\epsilon_{\max}$	12.6	10.5	13.3	15.6	12.8	16.2	16.3
$\lambda_F$ , nm	532	480	542	496	501	502	513
$\nu_S$ , $\text{cm}^{-1}$	6210	3490	4020	2110	1920	2860	3080
<b>P-Te</b>							
$\lambda_A$ , nm	373	398	422	427	433	425	427
$\lambda_e$ , nm	516	702	566	567	583	543	550
$\epsilon_{\max}$	15.3	10.9	14.6	17.9	14.9	19.8	19.8
$\lambda_F$ , nm	510	440	483	465	474	460	468
$\nu_S$ , $\text{cm}^{-1}$	7210	2390	2990	1910	1990	1790	2050

Dynamic nature of MSPs has been examined by the “*end-capping experiment*” at which the **pybox-Th** monotopic ligand has been added to the solution of Zn<sup>2+</sup>/**P-Bt** MSPs ( $r = 1$ ). The occurrence of a new absorption band with  $\lambda_A$  equal to that of the **pybox-Th-Zn<sup>2+</sup>-pybox-Th** dimer proves a partial disassembly and/or end-capping of MSP chains with **pybox-Th** ligands as well as the formation of the butterfly dimer species on account of the MSP chains. In any case, this result proves constitutional dynamics of the **pybox** type Zn-MSPs the dynamics of which in solution is so fast that it disallows a GPC/SEC analysis of these dynamers.



**Figure 5.** Photoluminescence spectra of  $Mt^{2+}/P-Th$  systems as a function of the ratio  $r$ .

**Table 3.** Comparison of the fluorescence data for dissolved and solid *pybox* Zn-MSPs ( $r = 1$ ); emission maxima ( $\lambda_F$ , nm) and quantum yields ( $\phi_F$ , %).

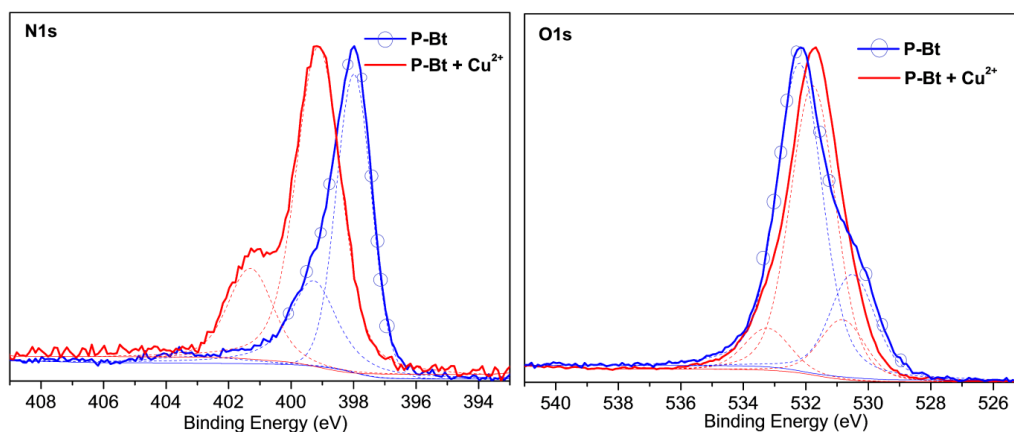
	$Zn^{2+}/P-Th$		$Zn^{2+}/P-Bt$		$Zn^{2+}/P-Te$	
	$\lambda_F$ , nm	$\phi_F$ , %	$\lambda_F$ , nm	$\phi_F$ , %	$\lambda_F$ , nm	$\phi_F$ , %
solution	434	22.2	542	34.2	483	17.4
film	614	2.02	635	1.99	618	1.51

### Characteristics of solid MSPs

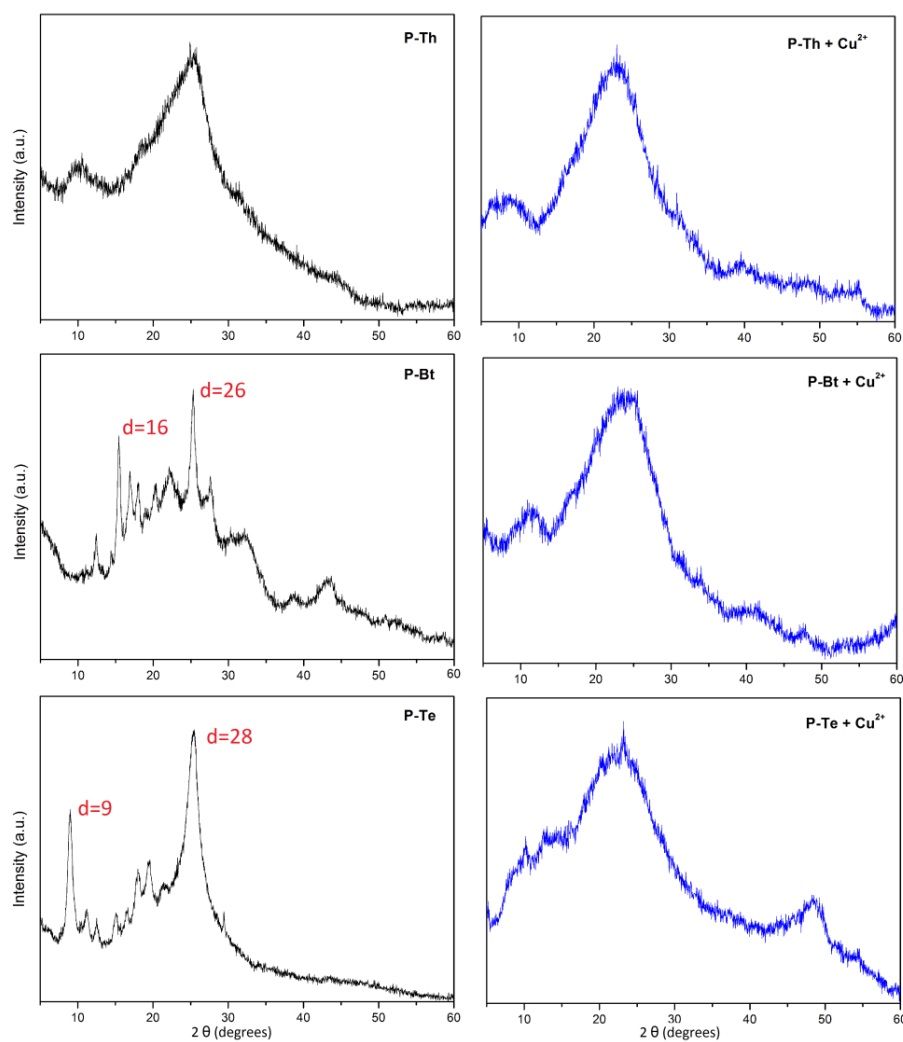
The luminescence data for *pybox* Zn-dynamers (Table 7) indicate a significant red shift of the emission band when going from solution to the solid state. The highest shift (+180 nm) is observed for  $Zn^{2+}/P-Th$  polymer and the lowest one (+90 nm) for  $Zn^{2+}/P-Te$  polymer. It is worth noting here that also in this respect the *pybox* MSPs substantially differ from *tpy* MSPs which typically show a small red or even blue shift accompanying solidification (drying).<sup>9, 8</sup>

Oxazoline rings of the *pybox* end-group can coordinate to a metal ion by N or O atom. Coordination mode of this moiety has been determined by the X-ray photoelectron spectroscopy (XPS) using free unimers and their  $Cu^{2+}$ -MSPs (see

example in **Fig. 6**). A shift of the N1s peak to higher binding energy (1.1–2 eV) was observed for all systems, which proves a decreases in electron density on the nitrogen atoms of pyridine and oxazoline rings caused by the electron band



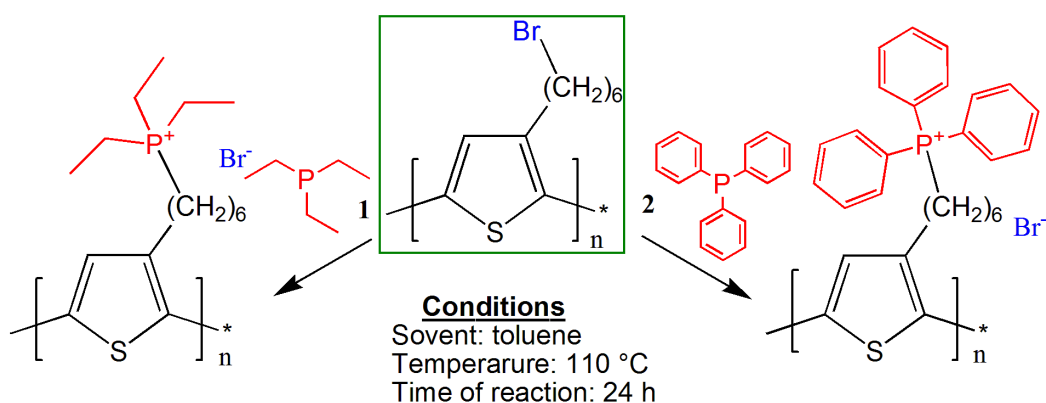
**Figure 6.** XPS spectra of **P-Bt** unimer and **Cu<sup>2+</sup>/P-Bt MSP** ( $r = 1$ ).



**Figure 7.** XRD spectra of **pybox** unimers (left) and their **Cu-MSPs** ( $r = 1$ , right).

withdrawing effect of  $\text{Cu}^{2+}$  ions. In contrast, the O1s XPS spectra showed the shift to lower binding energy. This result clearly indicates predominant coordination of the oxazoline rings through nitrogen atoms.

The solid-state structures of prepared Cu-MSPs were also investigated by the XRD method. As can be seen (**Fig.7**) the XRD patterns of Cu-MSPs do not exhibit any sharp reflection but only extensive broadening of peaks indicating the amorphous character of self-assembled Cu-MSPs. On the other hand, the **pybox** unimers with two thiophene rings gave sharp reflections corresponding to the  $d$  spacing of 5.7 and 3.5 Å for **P-Bt** and 10 and 3.3 Å for **P-Te**.



**Scheme 4.** Polythiophene polyelectrolytes with phosphonium side groups.

### Polythiophene polyelectrolytes with phosphonium side groups

The polythiophene polyelectrolytes have been prepared using the polymer modification approach (**Scheme 4**). First poly[3-(6-bromohexyl)thiophene]s of different regioregularity (tuned by polymerization temperature regime) were prepared by polymerizations catalyzed by  $\text{Ni}(\text{dppp})\text{Cl}_2$ . The obtained polymers were characterized (**Table 4**) and then modified by reactions with phosphates. The modification is supposed to remain intact the polymer main chains. Thus the molar mass and regioregularity of precursor polymers were applied to the corresponding polyelectrolytes with ionic side groups.

The extent of the precursor polymers' transformation into polyelectrolytes (CPEs) was examined by NMR spectroscopy (**Figure 8**). The signal at 3.43 ppm of protons in  $\text{CH}_2\text{Br}$  group (**red spectrum**) is absent in the (black) spectrum of **PH-EtP<sup>+</sup>**, in which also new signal at 1.2 ppm of the protons of  $\text{CH}_3$  groups appears. In contrast, the (**green**) spectrum of **PH-PhP<sup>+</sup>** shows only attenuated signal of  $\text{CH}_2\text{Br}$  groups (3.43 ppm). The degree of ionization determined from

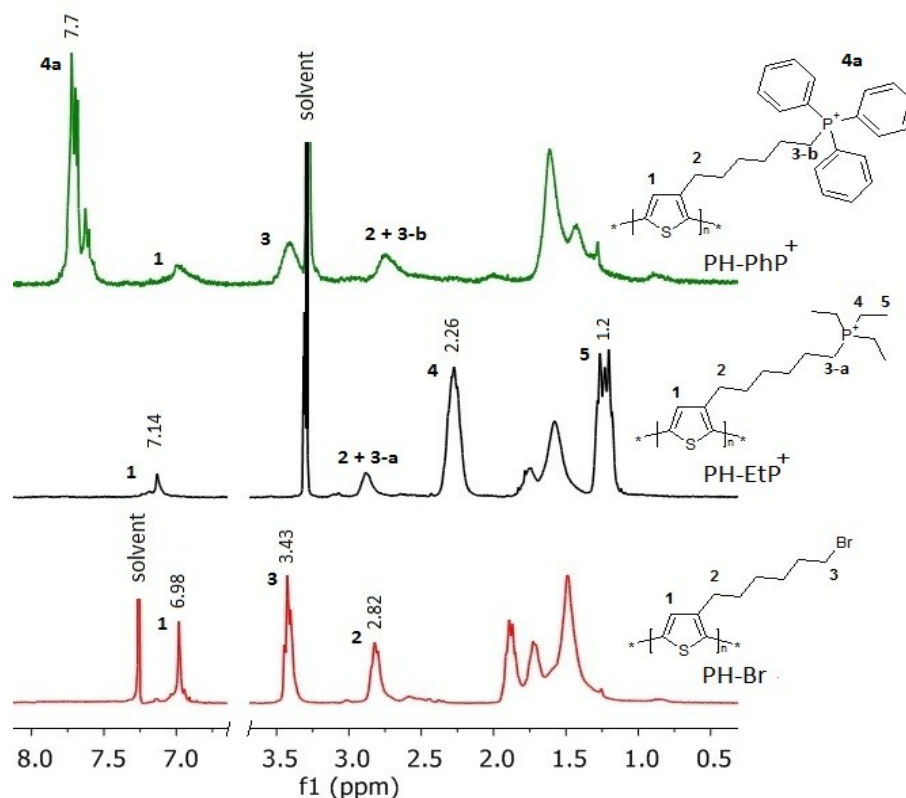
the NMR spectra of **-PhP<sup>+</sup>** polymers was found to be 0.5 for **PL-PhP<sup>+</sup>**, 0.55 for **PM-PhP<sup>+</sup>** and 0.57 for **PH-PhP<sup>+</sup>** while 1.0 for all **-EtP<sup>+</sup>** polymers.

**Table 4.** Polymerization and spectroscopic data for precursor polymer of the low (**PL-Br**), medium (**PM-Br**) and high (**PH-Br**) regioregularity. *T* is polymerization temperature; *M<sub>w</sub>* - weight-average and *M<sub>n</sub>* - number-average molar mass; *D* - dispersity; *rr* - H-T regioregularity;  $\lambda_A$ ,  $\lambda_e$  and  $\lambda_F$  wavelengths of the absorption maximum, absorption edge and emission maximum, respectively,  $\epsilon_{max}$  molar absorption coefficient for  $\lambda_A$  ( $m^3 mol^{-1} cm^{-1}$ );  $\nu_S$  Stokes shift ( $cm^{-1}$ );  $E_g$  - band-gap calculated from  $\lambda_e$  and;  $\phi_F$  - fluorescence quantum yield.

Sample	<i>T</i> , °C	<i>M<sub>w</sub></i> kg/mol	<i>M<sub>n</sub></i> kg/mol	<i>D</i>	<i>rr</i> %
<b>PL-Br</b>	65	7.20	4.6	1.6	62
<b>PM-Br</b>	25	11.8	6.8	1.7	78
<b>PH-Br</b>	5	13.2	8.7	1.5	94

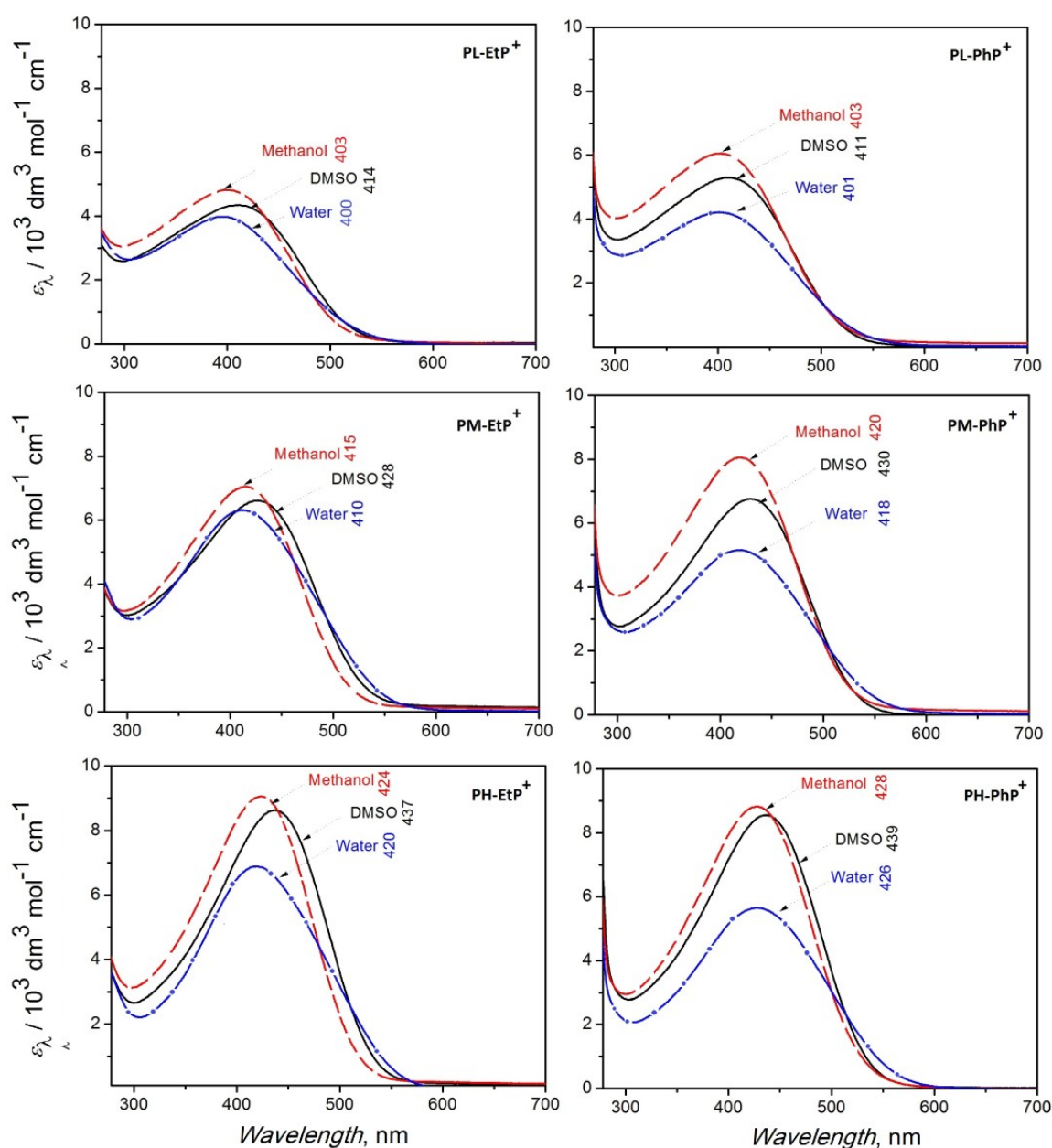
  

Sample	$\lambda_A$ nm	$\lambda_e$ nm	$E_g$ eV	$\epsilon_{max}$ $m^3 mol^{-1} cm^{-1}$	$\lambda_F$ nm	$\phi_F$ %	$\nu_S$ ( $cm^{-1}$ )
<b>PL-Br</b>	408	520	2.38	7.9	572	10	7030
<b>PM-Br</b>	417	535	2.31	9.6	576	11	6620
<b>PH-Br</b>	426	540	2.29	10.8	580	15	6230



**Figure 8.**  $^1H$  NMR spectra of the precursor polymer **PH-Br** ( $CDCl_3$ , r.t) and corresponding CPEs **PH-EtP<sup>+</sup>** and **PH-PhP<sup>+</sup>** (both measured in  $CD_3OD$ , r.t).

The UV/vis and luminescence spectra of prepared CPEs (**Figure 9, Table 5**) exhibit significant solvatochromism as well as dependence on the polymer regioregularity not only of the positions the absorption and emission maxima but also of the values of the molar absorption coefficient and quantum yield of luminescence. Surprisingly, the solvent order observed for  $\lambda_f$ : water > DMSO > methanol is different from the order: DMSO > methanol > water observed for the  $\lambda_A$  values. As a result, the Stokes shifts obtained for aqueous solutions are considerably higher than the shifts for the other two solutions, which indicate high complexity of the relaxation processes in excited molecules of our CPEs.



**Figure 9.** UV/vis spectra of PHT-EtP<sup>+</sup> and PHT-PhP<sup>+</sup> polyelectrolytes in indicated solvents.



**Table 5.** Spectral data of CPEs;  $\lambda_A$ ,  $\lambda_e$  and  $\lambda_F$  wavelengths of the absorption maximum, absorption edge and emission maximum, respectively;  $\epsilon_{\max}$  molar absorption coefficient;  $\nu_s$  Stokes shift;  $\phi_F$  fluorescence quantum yields measured in methanol (%).

Sample	Solvent	$\lambda_A$ nm	$\lambda_e$ nm	$\epsilon_{\max}$ $\text{m}^3 \text{mol}^{-1} \text{cm}^{-1}$	$\lambda_F$ nm	$\phi_F$ , %	$\nu_s$ ( $\text{cm}^{-1}$ )
PL-EtP <sup>+</sup>	Water	400	531	3.9	581	-	7790
	Methanol	403	513	4.8	564	11	7080
	DMSO	414	524	4.3	573	-	6700
PL-PhP <sup>+</sup>	Water	401	541	4.1	582	-	7760
	Methanol	403	522	6.0	569	10	7240
	DMSO	411	527	5.2	574	-	6910
PM-EtP <sup>+</sup>	Water	410	550	6.3	590	-	7440
	Methanol	415	518	7.0	567	16	6460
	DMSO	428	533	6.5	577	-	6030
PM-PhP <sup>+</sup>	Water	418	554	5.1	593	-	7060
	Methanol	420	525	8.0	571	14	6300
	DMSO	430	535	6.7	579	-	5990
PH-EtP <sup>+</sup>	Water	420	557	6.8	596	-	7030
	Methanol	424	518	9.0	570	22	6040
	DMSO	437	532	8.6	581	-	5670
PH-PhP <sup>+</sup>	Water	426	561	5.6	600	-	6810
	Methanol	428	531	8.8	576	15	5420
	DMSO	439	540	8.5	583	-	6210

Conjugated polyelectrolytes are able to electrostatically interact with various charged species such as metal ions, proteins or nanoparticles and thus significantly change their photophysical behavior. The fluorescence quenching, which can be best achieved by the addition of oppositely charged quenching species to a solution of the CPE, is of particular interest for the field of sensors. Therefore, the fluorescence quenching **PL-EtP<sup>+</sup>** and **PH-EtP<sup>+</sup>** polyelectrolytes by model quenchers such as  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  was performed using Stern-Volmer methodology. The results are shown in **Table 6**.

**Table 6.** Stern-Volmer constants  $K_{SV}$  for quenching the luminescence of **PL-EtP<sup>+</sup>** and **PH-EtP<sup>+</sup>** by  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$ .

CPEs/quencher	PL-EtP <sup>+</sup>		PH-EtP <sup>+</sup>	
	$\text{K}_3[\text{Fe}(\text{CN})_6]$	$\text{K}_4[\text{Fe}(\text{CN})_6]$	$\text{K}_3[\text{Fe}(\text{CN})_6]$	$\text{K}_4[\text{Fe}(\text{CN})_6]$
$K_{SV}$	$2.5 \times 10^4 \text{ M}^{-1}$	$1.44 \times 10^4 \text{ M}^{-1}$	$1.02 \times 10^5 \text{ M}^{-1}$	$4.48 \times 10^4 \text{ M}^{-1}$

## CONCLUSIONS

The aim of this work was development of novel conjugated polymers with tunable photophysical properties and improved processability from solutions. In particular, this work was focused on the development of (i) new linear unimers with chelate end-groups derived from the benzimidazole and oxazoline derivatives of pyridine that can be prepared from cheap chelidamic acid, which are able to undergo the self-assembly process with metal ions leading to the formation of MSPs, and (ii) polythiophene polyelectrolytes with phosphonium pendants that are soluble in aqueous mediums.

The synthesis routes to new monotopic ligands and corresponding ditopic unimers have been developed, which use a quite cheap and easily available chelidamic (4-hydroxypyridine-2,5-dicarboxylic) acid as the starting material. Various mono- and ditopic compounds with two different tridentate chelate groups (ion selectors): 2,5-bis(benzimidazol-2-yl)pyridine-4-yl (*bzimpy*) and 2,5-bis(4,5-dihydrooxazol-2-yl)pyridine-4-yl (*pybox*) have been prepared, characterized and assembled with various metal ions ( $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$ ). Monotopic ligands have been exploited for a detailed study of the process of coordination to metal ions and also as intermediates at the syntheses of linear unimers. Thiophene-2,5-diyl, bithiophene-2,5'-diyl, thienothiophene-2,5-diyl and terthiophene-2,5''-diyl units have been used as the central blocks of newly prepared unimers. Studies on the properties of *bzimpy*-based unimers and MSPs were limited because these compounds have shown relatively low solubility in organic solvents.

A detailed study on the coordination mode of monotopic *pybox* ligands proved that these ligands easily form  $[\text{MtL}_2]^{2+}$  species which are in a dynamic equilibrium with species  $[\text{MtL}]^{2+}$  and free ions, same as the ligands of terpyridine family. The *pybox* unimers also showed a good ability to coordinate to the above metal ions giving corresponding metallo-supramolecular polymers. The detailed study of the MSP assembly revealed three stages of this process, same as observed for bis(*tpy*) unimers: formation of "butterfly" dimers  $\text{U-Mt}^{z+}\text{-U}$  (U stands for a unimer species) at the  $\text{Mt}^{z+}/\text{U}$  mole ratios  $r$  up to ca 0.5, formation of longer MSP chains for  $r$  from above 0.5 to ca 1, and end-capping of MSP chains and their equilibrium depolymerization at  $r$  values above 1. The latter proves the constitutional-dynamic nature of the novel MSPs,

which is the fastest for Zn-dynamers and the slowest for Fe-dynamers. The dynamic nature of MSP chains has been also examined through the reaction of MSPs with monotopic ligands leading to the chains end-capped with these ligands.

The incorporation of different metal ions into MSP chains has been shown to result in significant differences in optical properties of the MSPs formed. The highest bathochromic shift of absorption maximum as compared to the free unimer was observed for  $\text{Cu}^{2+}$ -dynamers while the lowest shift for  $\text{Fe}^{2+}$ -dynamer for all *pybox*-based unimers. On the other hand, all  $\text{Fe}^{2+}$ -dynamers showed a new absorption band attributed to the metal to ligand charge transfer process (MLCT). Among all prepared MSPs, only  $\text{Zn}^{2+}$ -dynamers exhibited fluorescence while the other ones showed only fluorescence quenching. A good solubility of the *pybox*-based MSPs in organic solvents allowed preparation of thin solid films.

The other newly developed materials: cationic polythiophene polyelectrolytes have been prepared using the well established polymer modification approach. First poly[3-(6-bromohexyl)thiophene-2,5-diyl]s of different chain regioregularity were prepared by the Grignard metathesis polymerizations. The chain regioregularity has been tuned by varying the temperature regime of the polymerization process. So prepared precursor polymers were characterized and then transformed into cationic conjugated polyelectrolytes by simple quaternization reaction with triethylphosphine or triphenylphosphine. High solubility of these polyelectrolytes in water and water miscible solvents achieved thanks to the presence of phosphonium bromide pendant groups in their structure. Basic photophysical properties of these cationic conjugated polyelectrolytes were studied in water, methanol and DMSO solvents. These studies revealed solvatochromism of prepared polyelectrolytes and possibility of tuning their luminescence through the solvent polarity. The luminescence quenching by  $\text{K}_4[\text{Fe}(\text{CN})_6]$  and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  has been also studied and quantitatively described by Stern-Volmer constant. All experiments performed pointed to the principle influence of the main-chain regioregularity on the polymer properties except for its solubility in polar solvents.

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## List of Publications

1. S. Hladysh, D. Václavková, D. Vrbata, D. Bondarev, D. Havlíček, J. Svoboda, J. Zedník, J. Vohlídal, Synthesis and characterization of metallo-supramolecular polymers from thiophene-based unimers bearing pybox ligands, *RSC Adv.*, **2017**, *7*, 10718–10728.
2. S. Hladysh, D. Bondarev, J. Svoboda, J. Vohlídal, D. Vrbata, J. Zedník, Novel conjugated polyelectrolytes based on polythiophene bearing phosphonium side groups, *Eur. Polym. J.*, **2016**, *83*, 367–376.
3. O. Trhlíková, S. Hladysh, J. Sedláček, D. Bondarev, SEC-DAD - effective method for the characterization of  $\pi$ -conjugated polymers, *Materials Science Forum*, **2016**, *851*, 167–172.
4. P. Urbánek, A. di Martino, S. Hladysh, I. Kuřitka, A. Minařík, E. Pavlova, D. Bondarev, Polythiophene-based conjugated polyelectrolyte: Optical properties and association behavior in solution, *Synthetic Metals*, **2015**, *202*, 16–24.

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1. Sviatoslav Hladysh, Jiří Vohlídal: Novel conjugated polymers based on regioregular polyhexylthiophene bearing ionisable end groups. HOPV15, Rome, Italy, May 10 - 13, 2015. (Poster P1.154).
2. Sviatoslav Hladysh, Jiří Vohlídal: Novel metallosupramolecular polymers derived from terthiophenes with end-groups prepared from cheap chelidamic acid. ELECMOL 2014, Strasbourg, France, August 24 - 29, 2014. (Poster THU-129).

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## Abstrakt

Tato disertace se zabývá vývojem nových iontových konjugovaných polymerů se zlepšenou zpracovatelností z roztoků, konkrétně: (i) metalo-supramolekulárních polymerů (MSP) vzniklých samoseskupením konjugovaných unimerů (U, stavebních bloků) s ionty kovů  $Mt^{z+}$  do lineárních řetězců s alternačním uspořádáním stavebních jednotek  $[-Mt^{z+}-U]_n$  a (ii) polythiofenových polyelektrolytů s triethyl- a trifenyl- fosfoniovými bočními skupinami. Předností polyelektrolytů je jejich rozpustnost v ekologicky akceptovatelných rozpouštědlech, zejména alkoholech, optimálně ve vodě. Oproti tomu výhody MSP spočívají v termodynamické kontrole polymerizačního stupně jejich molekul díky reverzibilitě samoseskupovací reakce (polymerizace), kterou lze ovlivnit zejména výběrem rozpouštědla a teplotou. MSP tak obecně tvoří podstatně méně viskózní a tím i lépe zpracovatelné roztoky než kovalentní polymery.

Klíčovým krokem přípravy MSP je syntéza odpovídajícího(ch) unimeru(ů). V rámci této studie byla připravena serie nových unimerů s lineárními centrálními bloky oligothiofenového typu (mono-, bi-, ter- a thieno- thiofene –diyl bloky) a koncovými skupinami 6-bis(2-oxazolinyl)pyridine (*pybox*) a 2,6-bis(2-imidazolyl)pyridine (*bzimpy*). Unimery byly charakterizovány a použity k přípravě MSP. Je dobré zde zdůraznit, že výchozí surovinou pro přípravu chelátových koncových skupin unimerů byla levná, snadno dostupná chelidamová (4-hydroxypyridin-2,6-dikarboxylová kyselina).

Z bis(*pybox*) unimerů byly připraveny MSP s ionty  $Fe^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Eu^{3+}$  a  $Tb^{3+}$ . Protože bis(*bzimpy*) unimery vykazovaly značně nižší rozpustnost, byla jim věnována menší pozornost; studovány byly pouze jejich  $Fe^{2+}$  a  $Zn^{2+}$  MSP. Podrobné stadium odhalilo tři fáze samoseskupování iontů s unimery do MSP, což odpovídá zjištěním pro seskupování bis(*tpy*) unimerů s kovovými ionty: tvorba “motýlkových” dimerů  $U-Mt^{z+}-U$  (U je unimerní jednotka) pro  $Mt^{z+}/U$  molární poměry  $r$  do cca 0.5, tvorba delších MSP řetězců pro  $r$  od 0.5 do ca 1 a vazba nadbytečných iontů na konce MSP řetězců a rovnovážná depolymerizace řetězců pro  $r > 1$ . Finální depolymerizace potvrzuje konstitučně-dynamický charakter nových MSP. Nejrychlejší konstituční dynamika byla zjištěna pro Zn-dynamery, nejpomalejší pro Fe-dynamery, které jako jediné z připravených dynamerů vykazují přenosu náboje z kovového iontu na ligand (MLCT). Fotoluminescenční vlastnosti nových *pybox*- and *bzimpy*- MSP jsou kvalitativně

obdobné, jako vlastnosti *tpy*-MSP; pouze  $\text{Zn}^{2+}$ -MSP vykazují intenzivní fotoluminescenci, zatímco ostatní MSP vykazují jen zhášení luminescence s rostoucí koncentrací kovových iontů v systému.