

Scientific Report on the Short Visit Grant within the ORGANISOLAR Program of the European Science Foundation

Entitled: Conjugated Donor – Acceptor Metallo-Polymers as Photoactive Layer in Photovoltaic Devices.

Grantee

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Exchange Period: 12. July 2009 – 26. July 2009

Reference Number: 2977

Introduction Polymeric materials have been applied in photovoltaic devices, such as monolayer, heterojunction, and bulk heterojunction cells.^[1-4] In addition, dye-sensitized solar cells based on metal complex sensitizers and metal oxide semiconductors have also been fabricated and power-conversion efficiency up to 10% has been achieved.^[5, 6] These efficient solar cells are mainly based on ruthenium bipyridine complexes as the photosensitizing dyes, in which an electron is transferred from the d-orbital of the metal center to the p*-orbital of the bipyridine ligand upon photoexcitation.^[7] Subsequently, the electron is injected into the conduction band of TiO₂ and electric charges are generated. Furthermore ruthenium polypyridyl complexes have widely been employed as photosensitizers, emission sensitizers, and photocatalysts.^[8-10] We recently published the synthesis, photoluminescence and electroluminescence properties of some π -conjugated *bisterpyridines* zinc (II) coordination polymers, where the usage of polymeric sidechains lead to well soluble and film forming polymer.^[11-13] In recent years, π -conjugated polymer semiconductors with donor-acceptor (D–A) architectures have attracted considerable attention, since their electro-optical properties make them promising candidates for potential applications in the fields of organic electronics.^[14-16] A careful design and selection of the donor (D) and the acceptor (A) moiety enables the tuning of the intramolecular charge transfer (ICT) between the D and A subunits towards the desired optical and electronic properties. 2,2':6',2''-Terpyridine is one of the transition metal binding sites that is of particular importance for the construction of metallo-supramolecular polymers. Due to the prominent optical properties terpyridyl Zn(II) and Ru(II) moieties were introduced to optoelectronic applications by several research groups.^[17, 18]

We have synthesized a set of conjugated *bisterpyridines* connected by different spacer units, wherein both solely donor- (D), acceptor- (A) and mixed donor-acceptor (A-D-A and D-A-D) units were used. The general structures and examples of the systems are depicted in **Figure 1**. Despite the investigation of the D–A interaction, also the behaviour of different connection units between the terpyridine and the spacer unit was investigated (**7-10**).

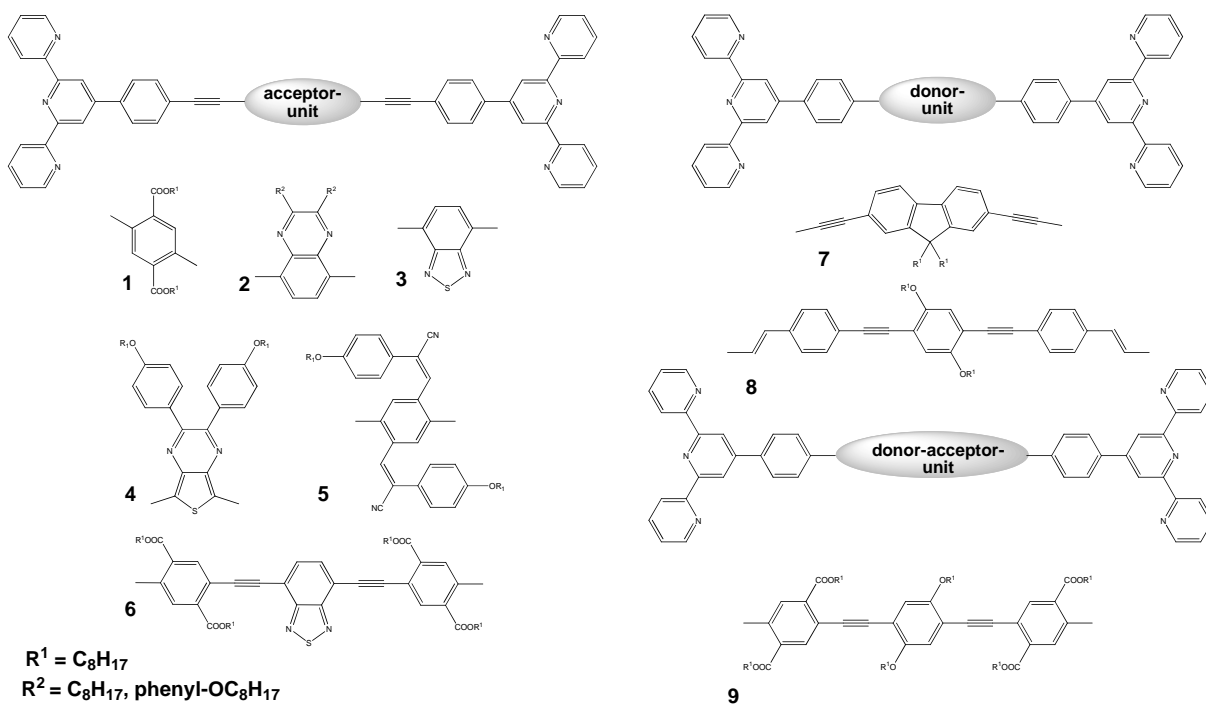
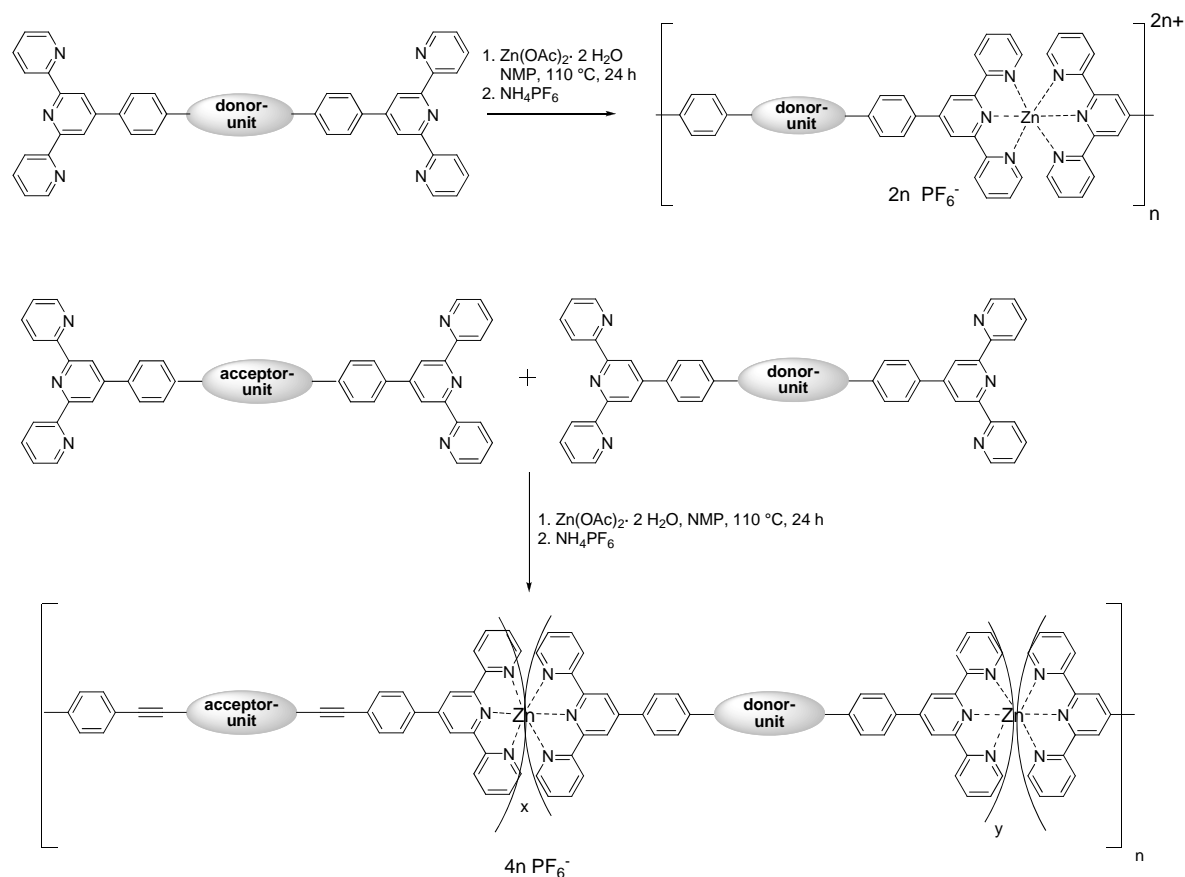


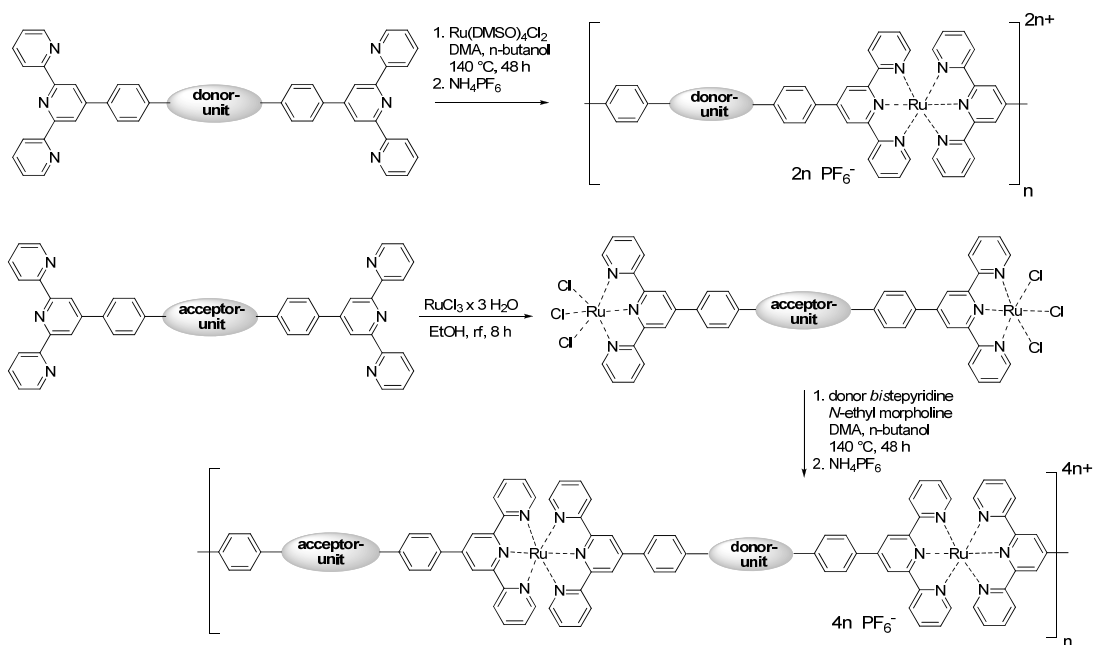
Figure 1. Schematic representation of the general structures of the investigated donor, acceptor and donor-acceptor *bisterpyridines*.

To synthesize zinc-containing polymers we reacted the respective bisterpyridine with $Zn(OAc)_2 \times 2 H_2O$ in NMP (*N*-methylpyrrolidone) for 24 h at 110 °C followed by anion exchange with excess of NH_4PF_6 .^[12] Using this protocol we produced, beside solely donor and acceptor also statistical copolymers of donor and acceptor systems (Scheme 1).



Scheme 1. Schematic representation of the synthesis of a homo- and a statistical donor – acceptor zinc-polymer.

When using ruthenium(II) instead of zinc(II) it is possible to synthesize, beside the homo and statistical, also alternating copolymers of donor and acceptor units (Scheme 2).



Scheme 2. Schematic representation of the synthesis of a ruthenium-homopolymer and an alternating donor – acceptor ruthenium-polymer.

These synthesized ligands and metal complexes have all been fully characterized by NMR- and UV-vis spectroscopy as well as elemental analysis, and the ligands additionally by MALDI TOF mass spectrometry.

Purpose During the visit we investigated the absorption and emission behavior of the polymers in thin films, under inert conditions. The ruthenium polymers are, caused by the MLCT transition and thereby an absorption maximum of around 500 nm, interesting systems for the construction of photovoltaic devices, whereas the zinc polymers exhibit absorption maxima around 400 nm, but strong photoluminescence, even in thin film. Therefore, they are promising candidates for the construction of light emitting devices. The electrochemical properties of the polymers were also subject of our studies in Prague, to enable an optimal device construction, by knowing the HOMO and LUMO level of the polymers and using suitable acceptor and electrode materials.

Results

Electrochemical Properties. With the help of cyclic voltammetry the energy levels of the highest occupied molecular orbital (HOMO), corresponding with the ionization potential, and of the lowest unoccupied molecular orbital (LUMO), corresponding with the electron affinity, can be estimated. The electrochemical properties of the *homo*-polymers (**Zn1 – Zn7, Zn9 and Ru7**) and copolymers (**coZn2-7** and **coRu2-7**) were obtained from thin films of the materials coated on Pt wires (0.1 M TBAPF₆ in CH₃CN; scan rate 50 mV·s⁻¹) are summarized in **Table 1**.

Table 1. Electrochemical properties of the *homo*-polymers (**Zn1 – Zn7, Zn9 and Ru7**) and copolymers (**coZn2-7** and **coRu2-7**).

polymer	$E_{1/2}^{\text{red}}$ [a]	$E_{\text{onset}}^{\text{red}}$ [b]	LUMO [eV]		E^{ox} [c] [V]	HOMO [c] [eV]	E_g^{ec} [c] [eV]	E_g^{opt} [d]
	[V]	[V]	$E_{1/2}$ [a]	E_{onset} [b]	(1/2;onset)	(1/2;onset)	(1/2;onset)	[eV]
Zn1	-1.34, -1.65	-1.26	-3.41	-3.49				2.85
Zn2	-1.33, -1.73	-1.26	-3.42	-3.49				2.78
Zn3	-1.42	-1.23	-3.33	-3.52				2.59
Zn4	-1.38, -1.66	-1.18	-3.37	-3.57				2.08
Zn5	-1.35	-1.22	-3.40	-3.53				2.73
Zn6	-1.36, -1.66	-1.20	-3.39	-3.55				2.33
Zn7	-1.33	-1.27	-3.42	-3.48				3.08
Zn9	-1.34, -1.68	-1.22	-3.41	-3.53				2.51
coZn2-7	-1.33, -1.73	-1.25	-3.41	-3.50				2.91
coZn3-8	-1.54	-1.10	-3.21	-3.65				2.76
coRu2-7	-1.38, -1.60	-1.27	-3.37	-3.48	0.89; 0.73	-5.64; -5.48	2.27; 2.00	2.15
Ru7	-1.39, -1.62	-1.25	-3.36	-3.50	0.89; 0.76	-5.64; -5.51	2.28; 2.01	2.13

[a] LUMO and HOMO levels were calculated from the measured first reduction/oxidation potential versus Fc/Fc⁺ according to eq.1. [b] LUMO and HOMO levels were calculated from the onset of the measured first reduction/oxidation potential versus Fc/Fc⁺ according to eq.1. [c] calculated from the $E_{1/2}; E_{\text{onset}}$ values. [d] $E_g^{\text{opt}} = h \cdot c / \lambda_{0.1\text{max}}$.

All zinc polymers (**Zn1 - Zn7, Zn9** and **coZn2-7**) exhibit reversible reduction peaks between -1.33 and -1.80 V. These peaks are attributed to the reduction of terpyridyl-based moieties.^[19-21] Furthermore, the majority of the metallo-polymers are showing distinct reduction waves at more negative potentials. As anticipated no significant oxidation processes are observed up to 1.5 V. Due to the stable d¹⁰ electron configuration of the Zn^{II} metal centers, oxidation is difficult to observe.^[11, 19] The LUMO levels estimated here are based on the first reduction wave and on the reference energy level of ferrocene, according to equation 1.

$$E_{\text{LUMO}} = [- (E_{1/2\text{red}} - E_{\text{reference}}) - 4.8] \text{eV} \quad (\text{Eq. 1})$$

$$E_{\text{HOMO}} = [- (E_{1/2\text{ox}} - E_{\text{reference}}) - 4.8] \text{eV}$$

The LUMO levels are ranging between -3.48 and -3.65 eV. Due to the absent oxidation potentials, the corresponding estimation of the ionization potential (HOMO) was not suitable by CV and, consequently, the calculation of the electrochemical band gap equally not. Therefore, the band gap of the metallo-polymers has been obtained from the UV-vis absorption spectra by extrapolating to the 0-0 transition of the longest wavelength absorption band. It is in the range of 2.08 to 3.08 eV and strongly influenced by the nature of the π -conjugated spacer unit. Considering this, the photophysical properties can be tuned by optimizing the chromophore, which has been shown especially with the small band gap of homo-polymer **Zn4**. The ruthenium polymers show, beside two reversible reduction peaks around -1.38 and -1.60 eV, one oxidation wave at 0.89 eV, corresponding to the oxidation of the Ru^{II} centre to Ru^{III}. Both types of metallo-polymers (using zinc or ruthenium) showed a reversible color change during reduction. Zinc polymers changed their color from yellow, over red to black, and ruthenium ones from red to black. The reversibility of these color changes makes them interesting systems for electro-optical measurements.

Photophysical Properties. Further investigation on the photophysical properties of both the *homo*-polymers **Zn1 – Zn7**, **Zn9**, **Ru7** and copolymers **coZn2-7** **coZn3-8** and **coRu2-7** was carried out by UV-vis absorption and photoluminescence spectroscopy both in solution and in thin film. The spectroscopic data of four representative polymers are summarized in **Table 2** and **Figures 2** and **3**.

In general, all the zinc-polymers showed – in agreement with the observations for the *bis*-terpyridines **1 - 7** and **9** characteristic absorptions between 270 and 450 nm, where the transitions at higher energy correspond to the terpyridine motive itself and the lower energy transitions to

absorptions of the whole π -conjugated system. As expected, the Zn^{II} cores do not participate in the transitions, in accordance to the filled d^{10} electron shell. A combination of **2** and **7** as donor-acceptor pair was chosen for *random*-copolymer **coZn2-7** because it exhibits a preferably large overlap of the absorption of the acceptor part with the emission of the donor unit. The position of the PL emission maximum of the donor *bis*-terpyridine **7** ($\lambda_{\text{PL}} = 403$ nm) is almost at the same wavelength as the π - π^* transition of the π -conjugated system of the acceptor system **2** (396 nm). Additionally, the extinction coefficients are in a comparable order of magnitude.

Table 2. Photophysical properties of *homo*-polymers (**Zn7**, **Ru7**) and *random*-copolymers (**coZn2-7** and **coRu2-7**).

polymer	$\lambda_{\text{abs,max}}^{\text{[a]}}$ [nm]		$\lambda_{\text{PL,max}}^{\text{[a]}}$ [nm]		$\epsilon \times 10^4^{\text{[a,b]}}$ [L·M ⁻¹ ·cm ⁻¹]	$\Phi_{\text{PL}}^{\text{[c]}}$	$\Delta v_{\text{af}}^{\text{[d]}}$ [cm ⁻¹]	$E_g^{\text{opt}}^{\text{[e]}}$ [eV]
	solution	film	solution	film				
coZn2-7	369, 320, 281	383, 344, 288, 234	432, 409(s)	523	11.25	0.81	4,000/7,000	2.91
Zn7	369, 321, 282	390, 340 322, 288, 235	424(s), 409	522	8.25	0.95	3,500/6,500	3.08
coRu2-7	505, 382, 338, 316, 289	501, 380(s), 334, 316, 278, 234(s)			11.50			2.15
Ru7	505, 383, 340, 320, 290	502, 363, 336, 318, 288, 234			5.30			2.13

[a] For all solution spectra: 10^{-6} M in DMF; (s) = shoulder. [b] Extinction coefficients at the lowest-energy absorption band; per repeating unit. [c] Absolute quantum yields in solution. [d] $\Delta v_{\text{af}} = 1/\lambda_{\text{a}} - 1/\lambda_{\text{f}}$; solution/film. [e] $E_g^{\text{opt}} = hc/\lambda_{0.1\text{max}}$; solution.

Also the absolute quantum yields (Φ_{PL}) of the materials were determined. In the case of the *homo*-polymer **Zn7**, an increase of Φ_{PL} in comparison to the ditopic terpyridine ligands **7** upon complexation was observed (**7**: $\Phi_{\text{PL}} = 0.77$; **Zn7**: $\Phi_{\text{PL}} = 0.95$). Also a redshift of $\lambda_{\text{PL,max}}$ of 20 nm was observed in solution on going from the ligand to the corresponding Zn complex. Such a behavior could be attributed to a charge transfer occurring within the ligands between the

electron-rich central chromophore and the electron-deficient metal-coordinated terpyridine moieties.^[18, 19] When comparing the absorption spectra of the zinc-metallopolymers it is obvious, that a bathochromic shift occurs when going from solution to film. In thin films the polymer chains lie open and flat and thereby enhancing π -stacking between neighboring chains and aggregate formation takes place. This contributes to lower the photoluminescence efficiency of the polymers in thin films compared to the solution. The enhanced planarization of the conjugated backbone gives rise to the bathochromic shift of the absorption and emission spectra of the polymers **Zn7** and **coZn2-7** in the solid state, shown in **Figure 2**, as compared to their solution samples. Beside the bathochromic shift also a new band at around $\lambda_{\text{abs}} = 340$ nm appears in case of both zinc-coordination polymers. This can be due to enhanced interaction in the thin

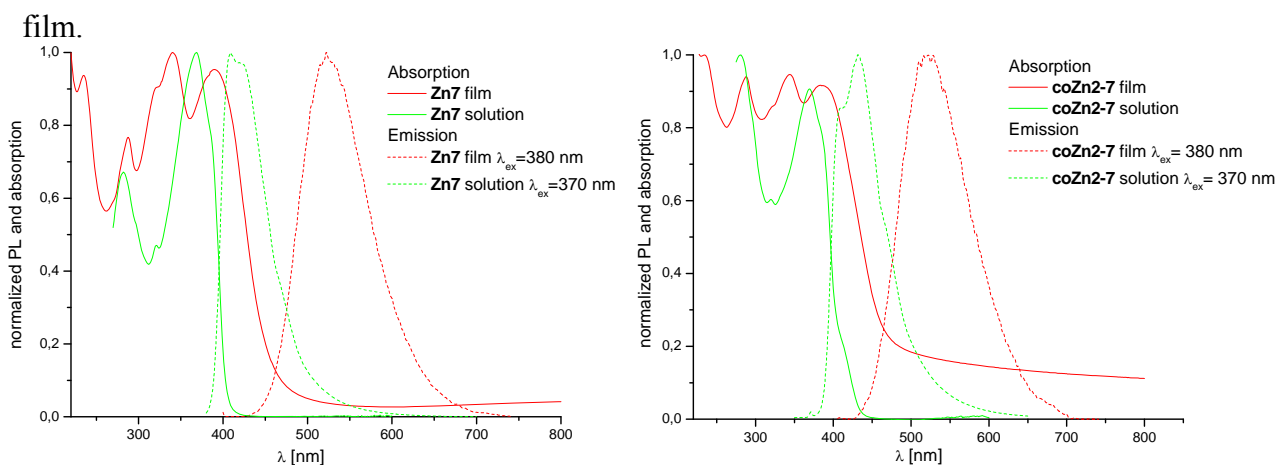


Figure 2. Normalized UV-Vis absorption (straight line) and photoluminescence (dashed line) spectra of **Zn7** and **coZn2-7** in solution (green) and thin film (red).

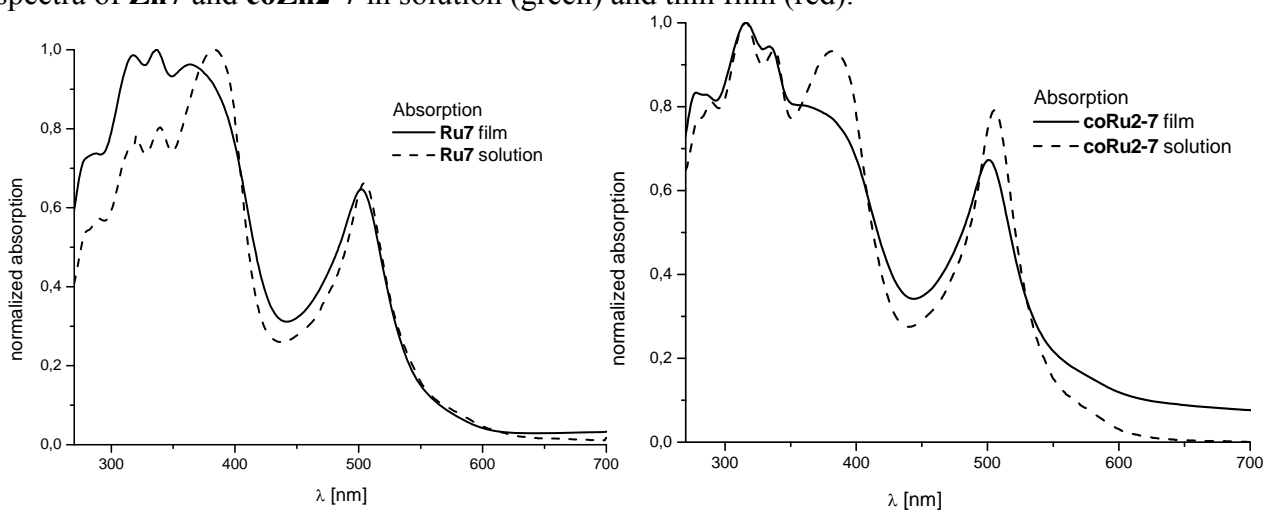


Figure 3. Normalized UV-Vis absorption spectra of **Ru7** and **coRu2-7** in solution (dashed line) and thin film (straight line).

In contrast, the ruthenium-coordination polymers **Ru7** and **coRu2-7** do not show any bathochromic shift, when comparing thin film and solution spectra. Here, the position of absorption does not change, just the intensities of the bands differ comparing solution and thin films. The absorption around $\lambda_{\text{abs}} = 380$ nm, representing the $\pi\text{-}\pi^*$ transition of the π -conjugated ligand, is more intensive in solution, whereas the signals at higher energy are especially in **Ru7**, less intensive.

Device Preparation

For the preparation of bulk heterojunction devices we needed to prepare homogeneous films of a thickness of about 100 to 150 nm. We applied different solvents, but unfortunately only DMF and DMSO showed adequate solubility behaviour. For adjusting the right thickness we prepared thin films on glass substrates cleaned before as described in the experimental section. The exact experimental setup is also described in the experimental part. The complete process of device preparation, including dissolving of the polymers, spincoating, absorption- and emission measurement, device preparation and device characterization was carried out under nitrogen atmosphere in a glove box. Thickness and roughness measurements were done under air after scratching the film. All solutions were filtered through a 0.45 μm PTFE filter before spincoating. Using the zinc polymers **Zn7** and **coZn2-7** a concentration of 20 mg/mL in DMF was achievable in an easy way. Spincoating the solutions using 1000 rpm for 100 s resulted in films with a thickness of 154 nm (**Zn7**) and 100 nm (**coZn2-7**), respectively.

Caused by the lower solubility of the ruthenium polymers we started with concentrations of 10 mg/mL in DMF. When using these solutions and the same parameters for spincoating as before we could produce films of a thickness of 32 nm (**Ru7** and **coRu2-7**). Also an adjustment of the rotation speed to 500 rpm and 750 rpm, respectively and a slow acceleration led only to thicknesses of around 66 nm and also the quality of the films decreased. (**Table 3**)

Thus, we had to increase the concentration of the polymer. For the homopolymer **Ru7** it was possible to achieve a concentration of 20 mg/mL in DMF, for the co-polymer **Ru2-7** a DMF/DMSO mixture had to be used. Spincoating of the higher concentrated solutions resulted in smooth films with thicknesses around 140 nm.

Table 3. Parameters used for the spincoating of polymer solutions.

Polymer	c [mg/mL]	solvent DMF/DMSO v/v	spincoating parameters		thickness [nm]
			speed [rpm]	acceleration/time [s]	
Ru7	10	1/0	1000/0	100	32
Ru7	10	1/0	750/7	100	65
Ru7	10	1/0	500/2	100	66
Ru7	20	2/1	1000/0	100	143
coRu7	10	1/0	1000/0	100	32
coRu7	20	1/0	1000/0	100	103

We could confirm the smoothness of the films by 3D profilometer measurement, as exemplarily shown for **coRu2-7** in **Figure 4**.

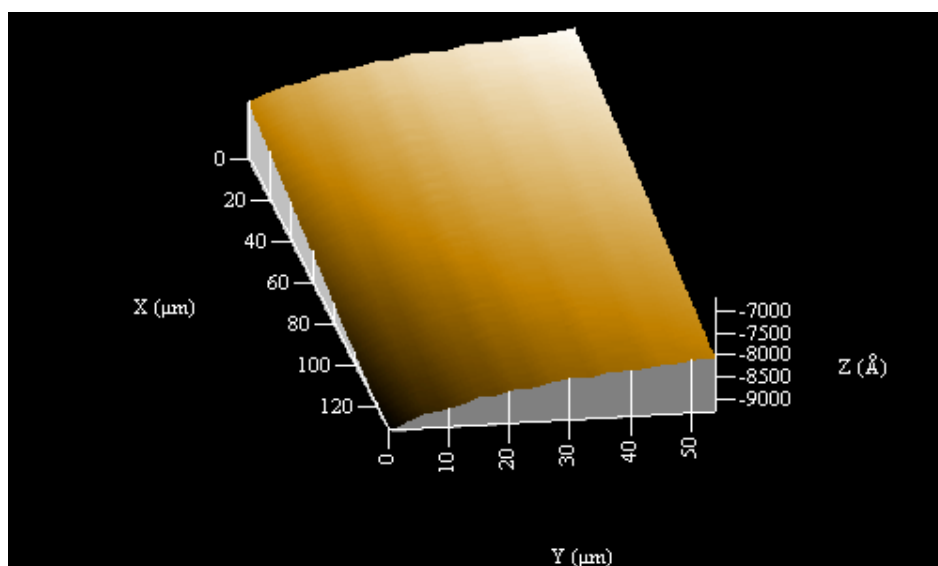


Figure 4. 3D profilometer image of the surface of a spincoated **coRu2-7** film.

For the preparation of bulk heterojunction solar cells a suitable acceptor is required to enable charge separation after excitation of the polymer by light. The most common used material therefore is PCBM[60]. Unfortunately PCBM[60] does not show sufficient solubility in the solvents used for spincoating the pristine polymer films, so different solvent mixtures were tried out. Finally, 20 mg/mL solutions of PCBM[60] in chlorobenzene were prepared and mixed with the solutions of the polymers. Using this procedure polymer:PCBM[60] mixtures 1:1 and 1:2 were prepared and spincoated using 1000 rpm for 100 s. The so obtained films were ocularly very homogeneous. But measuring the thickness and roughness using a profilometer revealed a very rough surface.

Table 4. Parameters used for the spincoating of polymer:PCBM[60] solutions.

polymer	c polymer [mg/ml]	solvent polymer DMF/DMSO v/v	mixture polymer:PCBM[60]	thickness [nm]
Ru7	20	2/1	1:1	600
Ru7	20	2/1	1:2	600
coRu7	20	1/0	1:1	600
coRu7	20	1/0	1:2	600

Spincoating parameters always 1000 rpm/100 s

As visible in **Figures 5** the spincoated films consists of phase separated areas with a distance of 3-5 μm , a thickness of about 3 μm and a height of 600 nm.

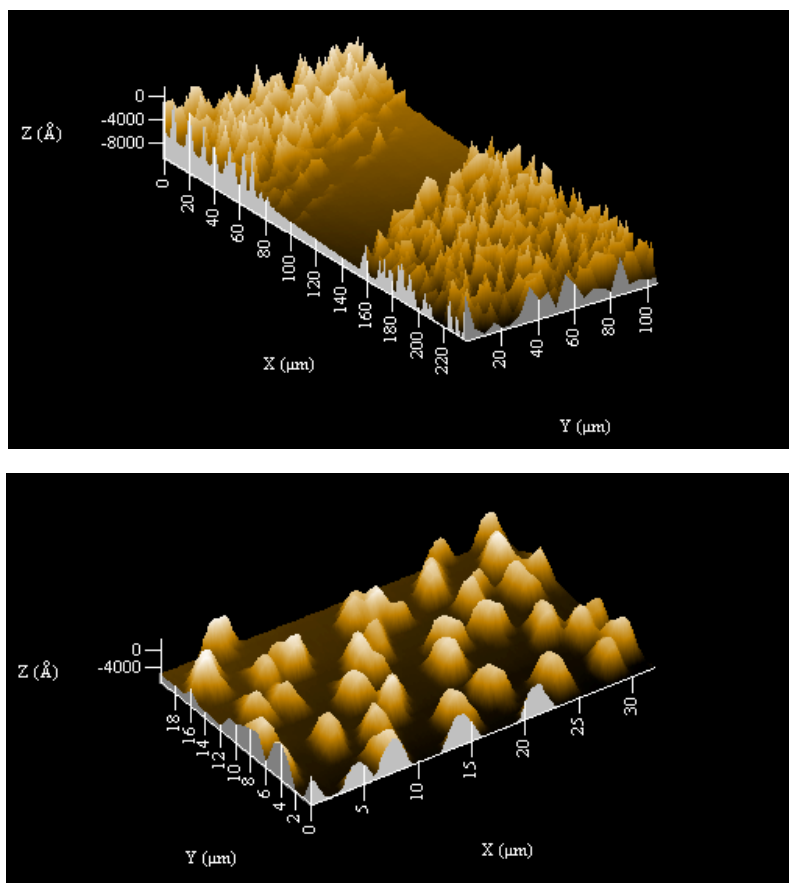


Figure 5. 3D profilometer image of the surface of a spincoated **coRu2-7/PCBM[60]** (1:2) film using chlorobenzene as solvent for PCBM.

Unfortunately the phase separated regions do not grow from a continuous layer of polymer:PCBM[60] mixture, but are completely separated from each other, so shortcuts would probably take place after deposition of the top electrode. Also thermal annealing could not improve the quality of the films. When changing the spincoating speed to 2500 rpm indeed the height of the film was reduced to 300 nm, but still the phase separated areas remained as large as they were before.

So we tried out to use other solvent mixtures to obtain a better morphology of the spincoated films. When using 1,2-dichlorobenzene to dissolve PCBM[60] and mixing it with the polymer solutions in DMF, in a 1:1 and 2:1 ratio, we could again obtain a good solubility of both polymer and PCBM[60]. Spincoating these mixtures using the above mentioned conditions (1000 rpm, 100 s) we obtained again ocularly homogeneous films. When checking thickness and roughness we noticed an about 30 to 50 nm layer on the substrate, and on top of this again phase separated regions, but this time only with a height of 100 to 150 nm a distance of around 2 μm and a diameter of 3 μm . (**Figure 6**)

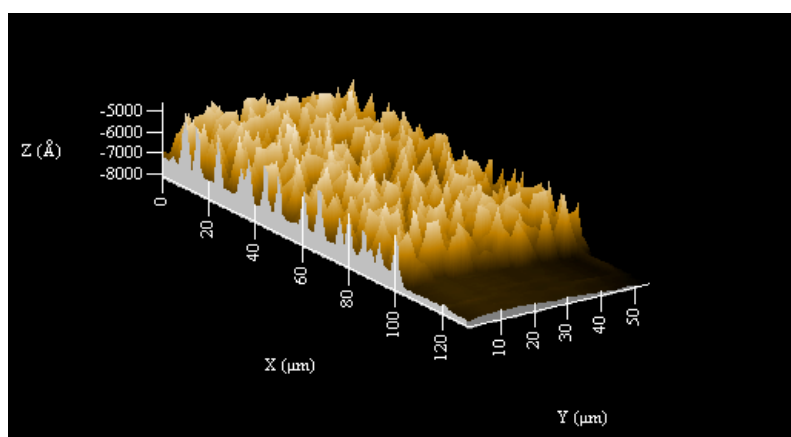


Figure 6. 3D profilometer image of the surface of a spincoated **coRu2-7/PCBM[60]** (1:2) film using 1,2 dichlorobenzene as solvent for PCBM.

Although the quality of the so obtained films was still low, with respect to the usage as photoactive layer in a bulk heterojunction solar cell, we used these conditions for the preparation of photovoltaic devices, especially with respect to the only two weeks working time. By investing some more time in the optimization of the solvent mixtures, the morphology of the film can be improved markedly. In order to achieve a smooth surface on top of this very rough polymer/PCBM[60] layer we decided to use a TiOx precursor, synthesized according to literature.^[22] TiOx is a promising candidate as an electron acceptor and transport material, as confirmed by its use in dye-sensitized cells,^[5, 23] hybrid polymer/TiO₂ cells^[24-26] and multilayer

Cu-phthalocyanine/dye/TiO₂ cells.^[27, 28] We prepared various substrates using different concentrations of the TiOx precursor in MeOH. When mixing the precursor solution and MeOH (1:10 ratio) we obtained a thickness of around 10 nm after hydrolysis for 15 min at 80 °C in air.

After this preliminary tests we used the previously prepared substrates consisting of a ITO layer and a PEDOT:PSS layer. The exact procedure for the preparation will be described in the experimental section. **Table 5** summarizes the composition of the prepared devices.

Table 5. Parameters used for the spincoating of polymer:PCBM[60] - and TiOx precursor solutions.

polymer	c polymer [mg/mL]	solvent polymer DMF/DMSO v/v	Mixture polymer:PCBM[60]	TiOx layer [nm]
Ru7	20	2/1	1:0	0
Ru7	20	2/1	1:2	0
Ru7	20	2/1	1:0	10
Ru7	20	2/1	1:2	10
Ru7	20	2/1	1:0	Blend 2:1 ^a
Ru7	20	2/1	1:0	Blend 1:1 ^a
coRu2-7	20	1/0	1:0	0
coRu2-7	20	1/0	1:2	0
coRu2-7	20	1/0	1:0	10
coRu2-7	20	1/0	1:2	10

a) A solution of the polymer was mixed with the precursor solution and spincoated in polymer:TiOx ratio of 2:1 and 1:1.

We prepared films of both pristine polymers (**Ru7** and **coRu2-7**) with and without a 10 nm layer of TiOx. Beside this, we mixed the polymer solutions with PCBM[60] solutions in a 1:2 ratio and prepared again films with and without a TiOx layer. Furthermore we mixed a solution of polymer **Ru7** with the precursor solution in a 2:1 and 1:1 ratio and spincoated also these films. All TiOx containing films were taken out of the glovebox after preparation and heated under air atmosphere. The films with a TiOx layer on top for 15 min and the blended films for 30 min at 80 °C. After this, the films were transported back into the glovebox and a LiF (2 nm) and Al (90 nm) layer was evaporated.

Device testing We tested the devices as photovoltaic module, measuring the electrical properties under dark and illumination using a Xenon lamp. Due to the very bad morphology the

devices did only show a very low photovoltaic effect. In particular, when using the structure PEDOT/polymer:PCBM[60];1:2/LiF/Al in most cases a short circuits occurred due to the very rough surface. This was the case for both investigated polymers (**Ru7** and **coRu2-7**). When using a TiOx layer on top of the polymer:PCBM[60] layer, less short circuits occurred and at least a very small photovoltaic effect was detectable. ($I_{SC} = 10^{-4} - 10^{-5}$ mA) For comparison reason also the pure polymers **Ru7** and **coRu2-7** were tested as photoactive layer (PEDOT/polymer/LiF/Al). The pure polymers did not show any measurable photovoltaic effect, but when using a layer of TiOx, this time not to smoothen the surface, but to act as an electron acceptor, a current of $I_{SC} = 10^{-3}$ mA and a voltage of $V_{OC} = 0.4$ mV was detectable. Therefore, we thought to directly mix the TiOx as an acceptor in a blend with the polymer. The so prepared devices showed indeed in particular a photovoltaic effect, but unfortunately also only in the magnitude of the before tested devices where just a TiOx layer was spincoated on top. Unfortunately also 50% of the tested cells were still short-cuttet. Most likely also the morphology of these TiOx:polymer blends is not optimal, but for time reason no further optimization could be carried out.

Experimental Section

Polymer thin films were prepared by spin-coating polymer solution onto silica fused substrates for optical studies or coated on Pt wire electrode by dipping for electrochemical measurements. UV-vis spectra were taken on a Perkin-Elmer Lambda 35 spectrometer, PL spectra using Perkin Elmer LS55 fluorimeter. Devices were supplied from a Keithley 237 source measure unit, which served for simultaneous recording of the current passing through the sample. Current-voltage characteristics were measured in dark and under irradiation recorded using a Keithley 237 source measure unit and 300W Xenon lamp(Oriel) with WG5 filter. The light intensity was measured by radiometer. Cyclic voltammetry (CV) was performed with a PA4 polarographic analyzer (Laboratory Instruments, Prague, CZ) with a three-electrode cell. Platinum(Pt) wire electrodes were used as both working and counter electrodes, and non-aqueous Ag/Ag⁺ electrode (Ag in 0.1 M AgNO₃ solution) was used as the reference electrode. CV measurements were made in solution of 0.1M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile in nitrogen atmosphere. Typical scan rates were 20, 50 and 100 mV s⁻¹. All measurements and film preparation were performed in a nitrogen atmosphere of a glove box. Layer thicknesses were measured outside the glove box using a KLA-Tencor P-10 profilometer.

Device Preparation Polymer solar cells were prepared according to the following procedure: The ITO-coated glass substrate was protected with Scotch tape at the areas where the electrodes should be present afterwards and the treated for 5 min in a 3 M FeCl₃ solution in 3 M HCl at 50 °C. Afterwards they are neutralized and washed with sat. NaHCO₃ and water. Subsequently, they were ultrasonicated in acetone and *iso*-propanol for 20 minutes, in between washed 12 times with distilled water, and finally put into ethanol and dried using nitrogen. Highly conducting poly(3,4-ethylenedioxylenethiophene):polystyrene sulfonic acid (PEDOT:PSS, Baytron P) was spin-cast (2500 rpm) with a thickness of 50 nm from aqueous solution with 5% DMSO. The substrate was dried for 15 min at 125 °C in air and then moved into a glove box for spin-casting the photoactive layer. Therefore, a 20 mg/mL solution of PCBM[60] (99.5% in 1,2-dichlorobenzene) was mixed with a 20 mg/mL solution of the polymer in DMF (or DMF/DMSO mixtures, see **Table 5**) This solution was passed through a 0.45 μm filter and was then spin-cast at 1000 rpm for 100 s on top of the PEDOT layer. Then, in particular the TiOx precursor solution was spin-cast on top of the polymer:fullerene composite layer. Subsequently, during 15 min at

80 °C in air the precursor converted to TiO_x by hydrolysis. The polymer:TiO_x blends were produced by mixing the polymer solution with the TiO_x precursor solution in different ratios and subsequently drying for 30 min at 80 °C under air. 5 nm LiF and 80 nm thick Al electrodes were vacuum-evaporated on the top of polymer films. Typical active areas were 12 mm²

Acknowledgements. I thank the European Science Foundation - Organisol for this grant. The colleagues in Prague, especially Vera Cimrová, Martin Lin and Adam Purkrt, are acknowledged for their help, the valuable discussions and the friendly atmosphere. Furthermore the support of the Dutch Polymer Institute (DPI), the Ministry of Education, Youth and Sports of the Czech Republic (grant No.1M06031) and the Grant Agency of the Academy of Sciences of the Czech Republic (grant No. IAA4050409) is acknowledged.

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