SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF SOME CONJUGATED POLYMERS FUNCTIONALIZED WITH RUTHENIUM POLYPYRIDINE COMPLEXES

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ABSTRACT

A series of conjugated polymers functionalized with different ruthenium polypyridine metal complexes were synthesized by the palladium catalyzed reaction. Two conjugated polymer systems have been studied: 1. poly(phenylenevinylene) with bis(2,2':6',2"-terpyridine) ruthenium (II) on the mainchain and 2. quinoxaline based polymers with tris(2,2'-bipyridine) ruthenium (II). The ruthenium polypyridine complexes exhibit a long-lived metal to ligand charge transfer excited state which can enhance the photosensitivity of the resulting polymers. Different physical properties such as the photoconductivity and charge mobility in these polymers are also studied.

INTRODUCTION

Organic conjugated polymers and oligomers have been used as the active semiconducting layer in various organic-based thin film devices such as solid state laser materials,[1] organic transistors,[2] light emitting diodes,[3] photodiodes,[4] and electrode active materials.[5] They combine the electronic and photonic properties of traditional inorganic semiconductors and the synthetic and processing advantages of organic polymers. In addition, organic materials also enjoy the advantages of ease of structural design and modification. The physical properties, solubility, and processibility can be easily "tuned" by attaching different functionalities to the polymer backbone or side chain. When conjugated polymers are coupled with transition metal complexes, they are expected to exhibit new properties because many transition metal complexes have specific catalytic, redox, and photophysical properties. A polymer-metal complex is a metal complex containing a polymer ligand which presents a remarkably specific structure in which central metal ions are surrounded by an enormous polymer chain. Based on this polymeric ligand, the polymer-metal complex shows interesting and important characteristics. Most of the studies on polymer-metal complexes are directed toward their catalytic activities not only because they are excellent models for the metalloenzymes, but also lead to the development of highly efficient catalysts.[6]

Here, we report the synthesis and characterization of two series of conjugated polymers which contain polypyridine complexes. The first system is a poly(*p*-phenylenevinylene) (PPV) incorporating ruthenium terpyridine complexes $[Ru(tpy)_2]^{2+}$ in the polymer mainchain, while the second system is quinoxaline-based poly(*p*-phenylene) (PPP), which contains a ruthenium bipyridine $[Ru(bpy)_3]^{2+}$ metal complex. The chemistry and photophysics of ruthenium polypyridine complexes have been studied extensively.[7] They are well known photosensitizers because of the relatively long-lived metal-ligand charge transfer (MLCT) excited states. When incorporated into conjugated polymers, the ruthenium polypyridine complexes may act as

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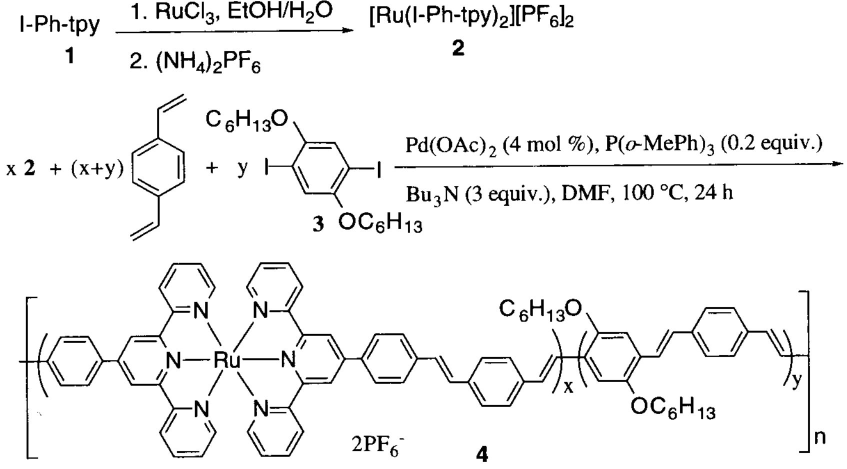
photosensitizers and thus enhance the photoconductivity. Moreover, the ruthenium complexes are also electrochemically active exhibiting a reversible $Ru^{II,III}$ redox process and a number of reductive ligand-centered processes.[8] In both polymer systems, the conjugated backbones were synthesized by the palladium catalyzed coupling reaction. This is a new approach to the design and synthesis of novel organic polymers for optoelectronic applications.



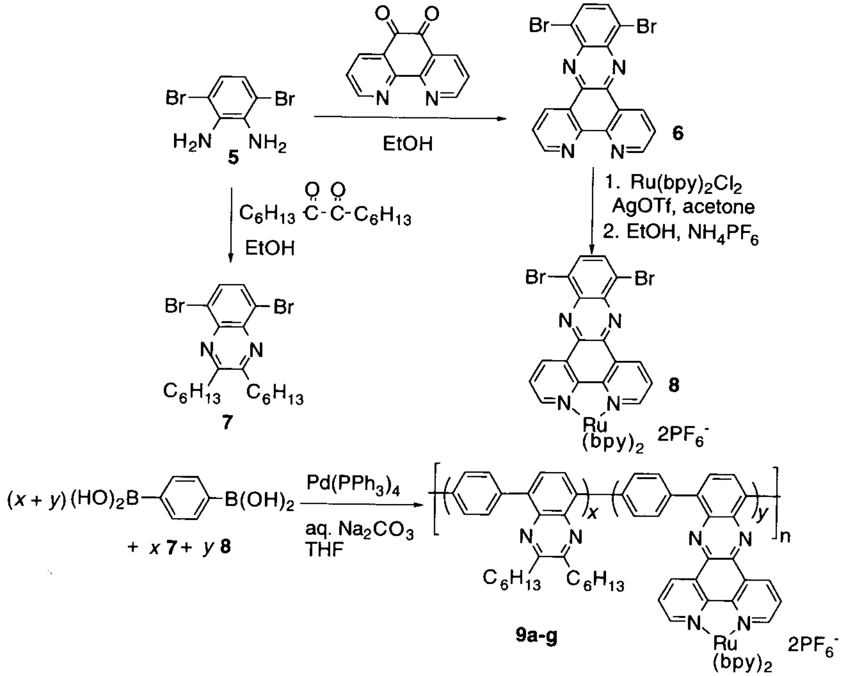
Scheme 1. Synthesis of $[Ru(tpy)_2]^{2+}$ containing PPVs.

EXPERIMENT

The synthesis of the monomers and polymers for the $[Ru(tpy)_2]^{2+}$ containing PPVs are shown in scheme 1.[9] Monomer **2** was synthesized by refluxing two equivalents of **1** with $RuCl_3$ and was isolated as the hexafluorophosphate salt. Polymers **4a**-**4e** were obtained in good yield by reacting 1,4-divinylbenzene with different ratio of **2** and **3** under standard Heck reaction conditions.[10] Dimethylformamide (DMF) was used as the solvent and the catalyst system was composed of palladium (II) acetate, tributylamine, and tri-*o*-tolylphosphine.

The synthesis of the quinoxaline-based monomers and polymers are shown in scheme 2. 5,8-Dibromo-2,3-dihexylqunioxaline **6** and 6,9-dibromodipyrido[3,2:*a*-2'3':*c*]phenazine **7** were synthesized by condensation reaction of **6** with tetradecane-7,8-dione and 1,10-phenanthroline-5,6-quinone, respectively. The direct complexation of **7** with *cis*-dichlorobis(2,2'-bipyridine)ruthenium dihydrate [*cis*-$Ru(bpy)_2Cl_2{\bullet}H_2O$] failed to give monomer **8**. Instead, monomer **8** was synthesized by refluxing an ethanol solution of $Ru(bpy)_2(acetone)_2(OTf)_2$ with **7**.[11] The quinoxaline based PPPs **9a**-**9g** were synthesized by the Suzuki coupling reaction using benzene-1,4-diboronic acid as comonomer.[12]

The photoconductivity of the polymers was measured according to the literature method with a lock-in-amplifier.[13] A 150 W xenon lamp with band pass filter was used as the light source. The charge mobility was determined by the conventional time-of-flight technique using a nitrogen laser (pulse energy = 120 μJ, pulse width = 3 ns) as the light source. The polymer film for measurement was prepared by casting the polymer solution on an indium-tin-oxide (ITO) glass. A thin layer of gold electrode (120Å) was coated on the polymer film by sputtering.



Scheme 2. Synthesis of quinoxaline-based PPPs.

RESULTS AND DISCUSSION

Some properties of the metal-containing polymers are summarized in Table I.

Table I. Properties of the metal containing polymers

Polymer	x	y	Reaction yield (%)	Inherent viscosity (dL/g)[a]	M_n[b]	Decomp. Temp. (°C)
4a	0.05	0.95	94	0.16	--	380
4b	0.1	0.9	98	0.38	--	375
4c	0.2	0.8	90	0.55	--	371
4d	0.3	0.7	94	0.41	--	386
4e	1	0	95	0.35	--	440
9a	1	0	87	--	26300	390
9b	0.9	0.1	76	--	9900	382
9c	0.8	0.2	69	--	11000	385
9d	0.7	0.3	51	--	8700	405
9e	0.6	0.4	48	--	6370	410
9f	0.5	0.5	49	--	5800	408
9g	03	0.7	41	--	15500	420

[a] Measured in DMF solution at 30 °C with concentration $c = 0.5$ g/dL.
[b] Number averaged molecular weight measured by GPC.

The metal containing PPVs **4a**-**4e** were synthesized by the Heck reaction in good yield. The reaction yield was not affected by the amount of the metal complex **2** present in the polymers. The quinoxaline-based PPPs **9a**-**9g** were synthesized by the Suzuki coupling reaction using $Pd(PPh_3)_4$ as the catalyst. The polymerization was carried out via a two-phase system with THF as the solvent and aqueous sodium carbonate solution as the base. In this system, the polymers exhibit lower yield and molecular weight when the proportion of the $Ru(bpy)_2(dppz)^{2+}$ (dppz = dipyridophenazine-6,9-diyl) unit is increased. One possible explanation is that the bulkiness of monomer **8** gives rise to its low reactivity. The low reactivity of monomer **8** was further confirmed from the synthesis of model compounds.

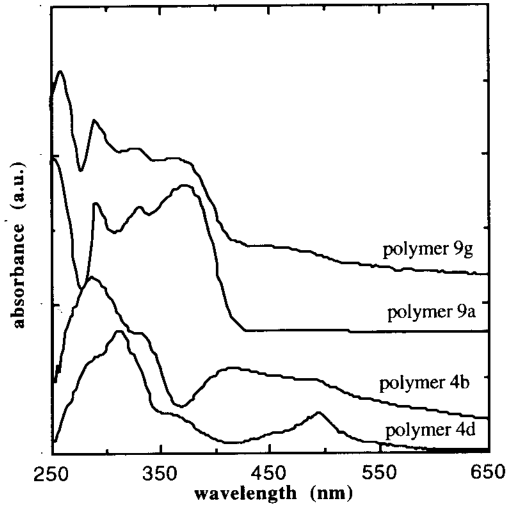


Fig. 1. UV/vis spectra of some metal containing polymers.

The UV-vis spectra of some polymers are shown in Fig. 1. Polymers **4b** and **9a** show absorption peaks at 420 and 380 nm, which are attributed to the electronic absorption of the conjugated PPV and PPP backbone, respectively. In polymers **4b** and **4d**, another peak was observed at ca. 500 nm due to the MLCT transition in the $[Ru(Ph\text{-}tpy)_2]^{2+}$ moiety. When the $[Ru(Ph\text{-}tpy)_2]^{2+}$ content in the polymer is increased, the intensities of the peak at 420 nm become lower because the extent of conjugation is decreased. For the PPP system, incorporation of monomer **8** into the polymer mainchain causes a small absorption peak to appear at 450 nm, which is due to the $Ru(bpy)_2(dppz)^{2+}$ unit. The intensity of this MLCT band increases further when the content of ruthenium complex in the polymer is increased.

The photoconductivity and charge transporting properties of the PPVs were also studied in more detail. Under the same applied electric field, the photoconductivity of the polymers increases with the $[Ru(Ph\text{-}tpy)_2]^{2+}$ content. Moreover, the photoconductivity of the polymers at different wavelength resemble their absorption spectra. This clearly shows the ruthenium terpyridine complexes increases the photoconductivity by enhancing the sensitivity.

The charge carrier mobility of the polymers was determined by the time-of-flight experiment. The transient photocurrent signal shows a featureless decay and the transient time cannot be determined directly from the photocurrent trace. The signal indicates that the charge transport is dispersive with non-Gaussian carrier distribution.[14] At room temperature, the hole mobilities of polymers **4b** and **4d** were determined to be 6.7×10^{-5} and 7.5×10^{-5} $cm^2V^{-1}s^{-1}$, respectively, which are both electric field and temperature dependent. These hole mobilities are three orders of magnitude higher than those of some phenyl-substituted PPVs.[15] These results clearly show the participation of the ruthenium complex in charge transport.

An Arrhenius plot of the hole mobility for polymer **4d** under different electric fields is shown in Fig. 2a. The graph indicates a thermally activated charge migration process with an activation energy of 0.19 eV at $E = 160$ kV/cm. The activation energy of polymer **4b** is slightly higher (0.22 eV) under the same applied field. The difference in activation energy may be related to the composition of the polymers. However, the exact reason for this is not clear. It was also found that the charge carriers are mainly holes as the electron mobilities are approximately one-tenth of the hole mobilities.

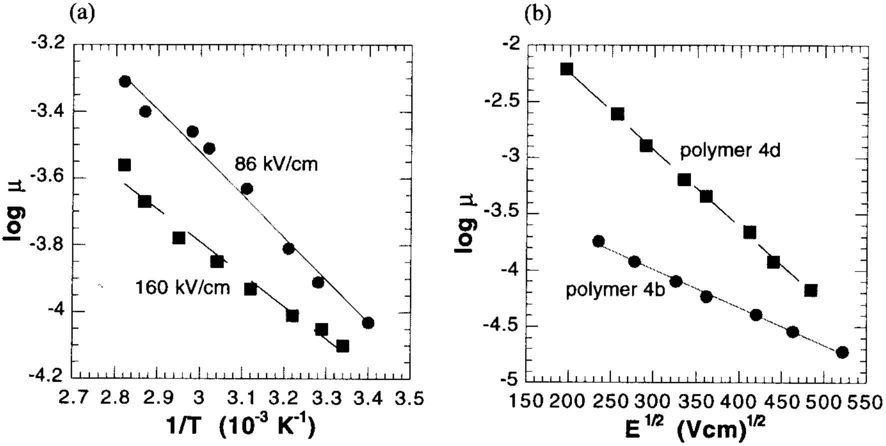


Fig. 2. (a) Temperature dependence of the hole mobility for polymer **4d** at different field strength. (b) Field dependence of the hole mobility at $T = 298$ K for polymer **4b** and **4d**.

Fig. 2b shows the hole mobilities of polymers **4b** and **4d** at room temperature. It can be seen that the log μ vs. $E^{1/2}$ plot shows a linear relationship with negative slopes. This interesting phenomenon can be explained by the presence of off-diagonal disorder in the hopping sites. The charge carriers have to jump against the field direction in order to open a faster route.[16] Other PPV derivatives[17] and triarylamine doped polycarbonate systems[18] reported in the literature also exhibit the same behavior.

CONCLUSIONS

We have synthesized two types of conjugated polymers functionalized with ruthenium polypyridine complexes using the palladium catalyzed reactions. Some photophysical properties of these polymers were studied by various characterization methods. It was found that the metal complexes can act as photosensitizers, as can be seen from the enhancement in photoconductivity. These polymers also exhibit modest hole carrier mobilities, whose migration is dispersive with non-Gaussian behavior. The charge mobilities are also affected by the amount of metal complex present in the polymer, indicating that the metal complex may also contribute to charge transport.

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