Title	Photoconductivity and charge transporting properties of metal-containing poly(p-phenylenevinylene)s
Author(s)	Chan, WK; Gong, X; Ng, WY
Citation	Applied Physics Letters, 1997, v. 71 n. 20, p. 2919-2921
Issued Date	1997
URL	http://hdl.handle.net/10722/42625
Rights	Creative Commons: Attribution 3.0 Hong Kong License

Photoconductivity and charge transporting properties of metal-containing poly(p-phenylenevinylene)s

Wai Kin Chan,[a)] Xiong Gong, and Wai Yue Ng

Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

A novel type of poly(p-phenylenevinylene)s which contain bis(2,2′:6′,2″-terpyridine) ruthenium (II) complexes has been developed. The absorption of the polymers at 500 nm was strongly enhanced by the metal complexes due to the presence of the metal–ligand charge transfer transition. The charge transportation is dispersive with hole carrier mobilities and activation energy of $\sim 7 \times 10^{-5}$ cm^2 V^{-1} s^{-1} and 0.20 eV, respectively, depending on the concentration of the metal complex. A log μ vs $E^{1/2}$ plot shows that hole mobilities decrease with increasing field, which suggests the presence of off-diagonal disorder in the hopping sites. © *1997 American Institute of Physics.* [S0003-6951(97)03046-5]

Extensive studies on organic semiconductors have led to the development of many new materials for optoelectronic applications.[1] Conjugated polymers is an interesting class of semiconducting materials which combines the electronic and photonic properties of traditional semiconductors and the processibilities of organic polymers.[2] Compared to their inorganic counterparts, organic polymers enjoy the advantages of ease of structural design and modification. The physical properties can be modified easily by attaching different functional groups to the polymer backbone. Poly(p-phenylenevinylene) (PPV) and its derivatives are among one of the most studied conjugated polymers. The potential of applying PPV to various types of optoelectronic devices has been proposed.[3] In our previous paper, we reported the synthesis of some functionalized PPVs which contain bis(2,2′:6′,2″-terpyridine) ruthenium (II) complex [Ru(Ph-tpy)$_2$]$^{2+}$ in the polymer backbone.[4] Polymers incorporated with transition metal complexes can serve not only as a photoconductor but also as the key component in advanced molecular electronics such as electroluminescent and photovoltaic devices. They are able to perform complex functions such as light harvesting and conversion of light into chemical or electrical energy.

Here, we report the detail studies of the photoconductivity and charge carrier mobilities of the [Ru(Ph-tpy)$_2$]$^{2+}$ containing PPVs. The ruthenium complexes exhibit a spin-allowed $d \rightarrow \pi^*$ metal–ligand charge transfer (MLCT) electronic transition which strongly enhances the absorption of the polymer in the visible region.[5] It is envisaged that by incorporating the [Ru(Ph-tpy)$_2$]$^{2+}$ as a photosensitizer to the polymer backbone, the sensitivies of the PPVs can be extended to longer wavelength. In addition, the [Ru(Ph-tpy)$_2$]$^{2+}$ complexes are electrochemically active exhibiting a reversible Ru^{II,III} oxidation process and a number of reversible reductive ligand-centered processes.[6] Therefore, the complexes are also potential charge carriers which are of fundamental importance to the design and construction of advanced electronic devices.

The structure of the metal-containing PPVs is shown in Fig. 1. Their physical properties are summarized in Table I.

Chemistry of the synthesis and detailed structural characterization have been described elsewhere.[4] Polymers I and II contain 19.4 and 45.8 wt. % of the [Ru(Ph-tpy)$_2$]$^{2+}$ complex, respectively. Such high concentration cannot be obtained by doping the ionic metal complexes into the organic polymer host as it usually leads to phase separation. Polymer I shows an absorption maxima and shoulders at 420 and 500 nm corresponding to the absorption of the backbone and the MLCT states, respectively. Polymer II only shows a MLCT absorption at 500 nm because the extent of the conjugation decreases as the content of [Ru(Ph-tpy)$_2$]$^{2+}$ is increased.

The samples for photoconductivity and charge carrier mobility measurement were prepared by casting a polymer solution on an indium–tin–oxide (ITO) glass and the solvent was evaporated slowly at elevated temperature. A semitransparent gold electrode (thickness = 120 Å) was coated onto the polymer film by sputtering. These polymers are good insulators with very small dark conductivity of the order of 10^{-15} Ω^{-1} cm^{-1}. However, when the polymers were exposed to visible light irradiation, large photocurrents were detected. The photocurrent was determined by measuring the voltage drop across a resistor resulting from the photocurrent passing through the polymer film. A 150 W xenon lamp with different band-pass filters ranging from 400 to 640 nm was used as the light source. Under the same applied electric field, the photoconductivity of the polymers increases with the [Ru(Ph-tpy)$_2$]$^{2+}$ content. The photoconductivity of the polymers at different wavelength resemble their absorption

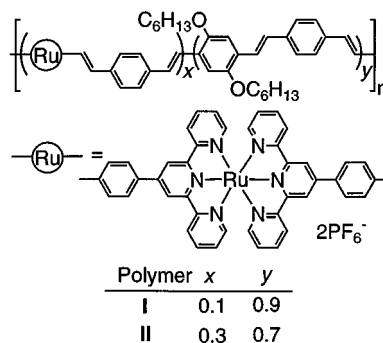| Polymer	x	y
I	0.1	0.9
II	0.3	0.7

FIG. 1. Structures of the ruthenium complex containing PPVs.

[a)] Electronic mail: waichan@hkucc.hku.hk

TABLE I. Physical properties of the polymers.

Polymer	$[Ru(Ph-tpy)_2]^{2+}$ content (wt %)	Δ_h[a] (eV)	σ[b] (10^{-12} Ω^{-1} cm^{-1})	μ_h[c] (10^{-5} cm^2 V^{-1} s^{-1})	μ_e[d] (10^{-6} cm^2 V^{-1} s^{-1})
I	19.4	0.22	1.4	6.7	5.4
II	45.8	0.19	5.6	7.5	5.8

[a]Activation energy for hole transport at $E = 160$ kV/cm.
[b]Photoconductivity at $E = 600$ kV/cm, $\lambda = 490$ nm.
[c]Electron mobility at 298 K, $E = 125$ kV/cm.
[d]Hole mobility at 298 K, $E = 125$ kV/cm.

spectra (Fig. 2). This clearly shows that the $[Ru(Ph-tpy)_2]^{2+}$ unit increases the photoconductivity of the polymers by enhancing the sensitivity.

The charge carrier mobility of the polymers was determined by using the conventional time-of-flight (TOF) experiment. Figure 3 shows the transient photocurrent profiles due to the hole transport of polymer I at different temperatures. Single pulse transient photocurrents were generated by a nitrogen laser [wavelength = 337.1 nm, pulse energy = 120 μJ, and pulse width full width at half-maximum (FWHM) = 3 ns]. The photocurrent pulse shows a featureless decay and the transient time t_T cannot be determined directly from the photocurrent trace. The transit time t_T means the time when the leading part of the carrier distribution reaches the collecting electrode. The signal indicates that the charge transport is dispersive with non-Gaussian carrier distribution. In a disordered solid with ''ideal'' non-Gaussian transport, the transient photocurrent is predicted by the equation $I(t) \propto t^{-(1-\alpha)}$ for $t < t_T$ and $I(t) \propto t^{-(1+\alpha)}$ for $t > t_T (0 < \alpha < 1)$, where α is the dispersion parameter.[7] The transit time and the hole mobility are defined by the intercept of the tangents approximating the current pulse at early and late times in the log I vs log t plot. Drift mobility μ was calculated according to the equation $\mu = L/t_T E$ where L is the film thickness and E is the applied electric field. At room temperature, the hole mobilities of polymers I and II were determined to be 6.7

$\times 10^{-5}$ and 7.5×10^{-5} cm^2 V^{-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.[8] This results clearly show the participation of the ruthenium complex in the charge transportation process.

An Arrhenius plot of the hole mobility for polymer II under different electric fields is shown in Fig. 4. 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 is lower than that of the triphenylamine-doped polycarbonate[9] and phenyl-substituted PPVs (~ 0.3–0.5 eV).[8] The activation energy of polymer I is slightly higher under the same applied electric field (Table I). The difference in activation energy may be related to the composition of the polymers. However, the exact reason for this is not clear. We postulate that the ruthenium complex may act as a hopping site when the charge migrates. It was also found that the charge carriers are mainly holes as the electron mobilities are approximately one-tenth of the hole mobilities.

The field dependence of the mobility can be expressed by[10]

$$\mu(E,T) = \mu_0 \exp\left(-\frac{\Delta_0}{kT_{\text{eff}}}\right) \exp\left(\frac{\beta E^{1/2}}{kT_{\text{eff}}}\right).$$

In this expression, μ_0 is the function of film composi-
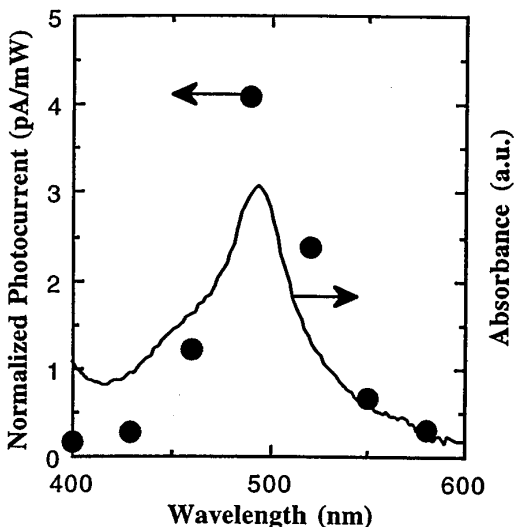

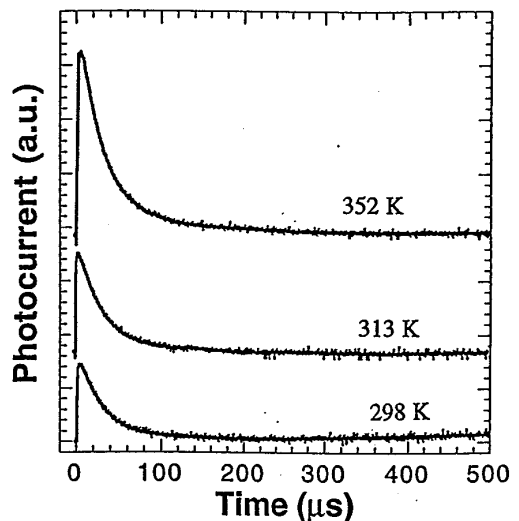FIG. 2. Normalized photocurrent and absorption spectrum of polymer II in the visible region.

FIG. 3. Transient photocurrent profiles due to hole transport for polymer I at different temperatures ($E = 125$ kV/cm).
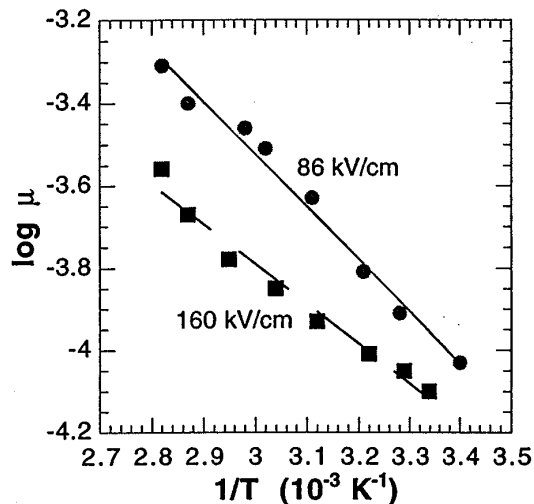
FIG. 4. Temperature dependence of the hole mobility at $E = 86$ and 160 kV/cm for polymer II.

tion, β is a constant coefficient, and T_{eff} is defined as $1/T_{eff} = 1/T - 1/T_0$ where T_0 is an experimental term which appears to characterize the transport system. Since an electric field reduces the barrier for jumps along the field direction, the drift mobility should increase by increasing the applied field. However the log μ vs $E^{1/2}$ plots for polymers I and II show a linear relationship with negative slopes (Fig. 5). This interesting phenomenon was also observed in some PPV derivatives,[11] 1,1-bis(di-4-tolylaminophenyl)cyclohexane-doped polycarbonate[12] and conjugated photorefractive polymers.[13] These 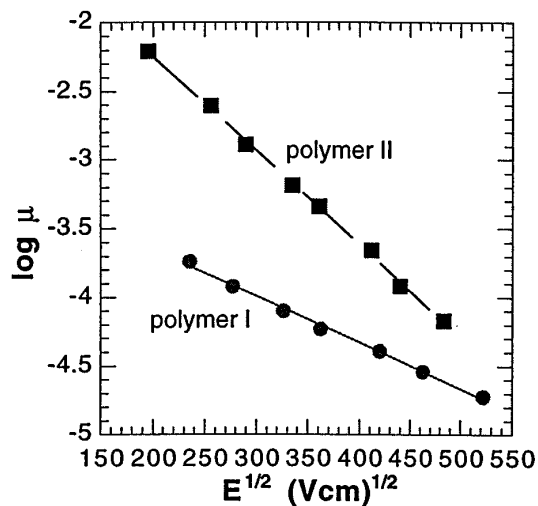observations are attributed to the presence of off-diagonal disorder in the hopping sites, which causes the charge carrier to jump against the field direction in order to open a faster route.[14]

In conclusion, we have investigated the photoconducting and charge transporting properties of transition metal complex-containing PPVs. From the TOF measurements, it was demonstrated that the hole migration is dispersive with non-Gaussian behavior. In addition, the charge mobilities are affected by the metal complex concentration, indicating that the metal complex plays an important role in the charge hopping process. Our polymers have demonstrated a new approach to the design and synthesis of organic polymers for optoelectronic applications because many transition metal complexes exhibit very interesting photophysical and redox properties.

FIG. 5. Field dependence of the hole mobility at $T = 298$ K for polymers I and II.

[1] *Electrical, Optical, and Magnetic Properties of Organic Solid State Materials*, edited by A. F. Garito, A. K.-Y. Jen, C. Y.-C. Lee, and L. R. Dalton, Materials Research Society Symposium Proceeding, Vol. 328 (Materials Research Society, Pittsburgh, 1994).

[2] *Handbook of Conducting Polymers*, edited by T. A. Skotheim (Dekker, New York, 1986), Vols. 1 and 2; *Electronic Properties of Polymers*, edited by J. Mort and G. Pfister (Wiley, New York, 1982).

[3] N. Tessler, G. J. Denton, and R. H. Friend, Nature (London) **382**, 695 (1996); F. Hide, M. A. Diaz-Garcia, B. J. Schwartz, M. R. Andersson, Q. Pei, and A. J. Heeger, Science **273**, 1833 (1996); N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, A. B. Holmes, Nature (London) **365**, 628 (1995); J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holmes, *ibid.* **376**, 498 (1995); G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, *ibid.* **357**, 477 (1992); J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *ibid.* **347**, 539 (1990).

[4] W. Y. Ng and W. K. Chan, Adv. Mater. **9**, 716 (1997).

[5] J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, and L. Flamigni, Chem. Rev. **94**, 993 (1994).

[6] M. Beley, J.-P. Collin, J.-P. Sauvage, H. Sugihara, F. Heisel, and A. Miehé, J. Chem. Soc. Dalton Trans. , 3157 (1991); E. C. Constable, A. M. W. Cargill Thompson, N. Armaroli, V. Balzani, and M. Maestri, Polyhedron **20**, 2702 (1992).

[7] H. Scher and E. W. Montroll, Phys. Rev. B **12**, 2455 (1975); G. Pfister and H. Scher, Adv. Phys. **27**, 747 (1978).

[8] A. Y. Kryukov, A. C. Saidov, and A. V. Vannikov, Thin Solid Films **209**, 84 (1992).

[9] G. Pfister, Phys. Rev. B **16**, 3676 (1977); M. Silver, G. Schönherr, and H. Bässler, Philos. Mag. **43**, 943 (1981).

[10] W. D. Gill, J. Appl. Phys. **43**, 5033 (1972).

[11] T. Takiguchi, D. H. Park, H. Ueno, and K. Yoshino, Synth. Met. **17**, 657 (1987); M. Gailberger and H. Bässler, Phys. Rev. B **44**, 8643 (1991).

[12] P. M. Borsenberger, L. Pautmeier, and H. Bässler, J. Chem. Phys. **94**, 5447 (1991).

[13] W. K. Chan, Y. Chen, Z. Peng, and L. Yu, J. Am. Chem. Soc. **115**, 11 735 (1993).

[14] M. Van der Auweraer, F. C. De Schryver, P. M. Borsenberger, and H. Bässler, Adv. Mater. **6**, 199 (1994).