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Electrochemical property of six novel conjugated conducting polymers and effecting characteristic with metal ions

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ABSTRACT

The electrochemical behaviour of six novel conjugated polymers containing phenothiazine moieties in main chain was studied in DMF with 0.1M tetrabutyl ammonium perchlorate (TBAP) by means of cyclic voltammetry (CV) on the glassy carbon electrode (GCE), as well as the electrochemical effect on Zn^{2+} and Hg^{2+} ions of the six polymers was investigated. The results show that these polymers all had well defined redox peaks, and the addition of metal ions had shifted the oxidation peak potential of the corresponding phenothiazine group to more cathodal position. By some electrochemical techniques, the electrode reaction processes were investigated in detail and their dynamic parameters were obtained. In addition, the energy levels of the frontier orbits of the six polymers were calculated and analyzed using CV.

KEYWORDS

Conjugated polymers;
Electrochemistry;
Dynamic parameters;
The energy levels;
Metal ions.

INTRODUCTION

Conjugated polymers have been intensively pursued owing to their potential application in organic conducting materials, light-emitting diodes (LEDs)[1-4], solid-state lasers[5-7], photovoltaic cells (PVs)[8, 9], biosensors[10], and transistors[11, 12]. Especially, Organic light emitting diodes (OLEDs) have been widely recognized as ideal starting devices for the fabrication of large area flat panel displays[13-15] since the first OLED was reported by Tang and Vanslyke in 1987[16]. At present, the OLED has been applied in a variety of products such as electronic and optoelectric commercial products. However, the development of high efficiency and color purity of organic semiconductor materials for blue and red OLEDs is still much in demand, which is to be currently resolved in the development of a satisfactory full color display based on OLEDs[17, 18].

Despite the plenty of fruitful results acquired in a vast body of work on organic-based materials, recently, there are strong motivations for chemists to incorporate metal units into organic and polymer structures[19-23]. The key interest in this research area is to determine the nature and extent of the electronic coupling between the metal and conjugated backbone units. Therefore, much attention has been focused on building and studying model complexes in which metal groups are tethered to conjugated fragments via different linkages, and examining the nature of the coupling in these systems[19-23]. However, the research on electrochemistry is still in its infancy and is worthy of attention.

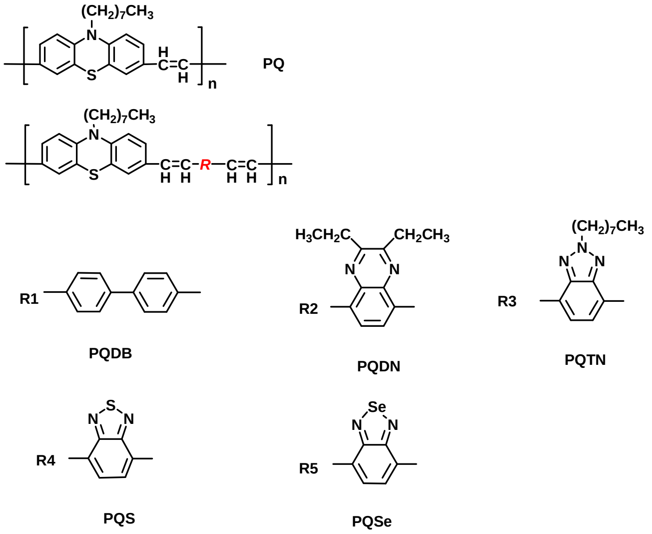
In addition, the electronic structure of the emitting materials is of vital importance to the characteristics of OLEDs. For example, the energy gap is defined by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the energy levels are required to match the work function of corresponding electrodes. The measurement of electrochemical redox properties provides a basis for estimating and assessing the electronic structure of the π-conjugated molecules[24].

In this study, we present the detailed electrochemical characters of six new conjugated polymers containing phenothiazine moieties in main chain and survey the electrochemical effect of the Polymers and metal ions.

EXPERIMENT

Materials and instruments

The polymers are self-synthesized in our lab by one of authors with Heck condensation polymerization and the detailed synthesis as well as fundamental characterization will be published elsewhere. The chemical structures of the polymers are shown in Scheme 1.



Scheme 1 : The chemical structure of the six polymers

The electrochemical investigation was performed on a CHI 650A electrochemistry workstation (CHI instrument Co, USA) with a three-electrode system. The glass carbon disk electrode (Ô=4mm), Pt wire electrode and saturated calomel electrode (SCE) were used as the working electrode, counter electrode and reference electrode respectively. Redox processes of the polymers in DMF were observed using 0.1M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. TBAP was prepared according to the literature[25].

RESULTS AND DISCUSSION

The electrochemical behavior of six polymers at GC electrode

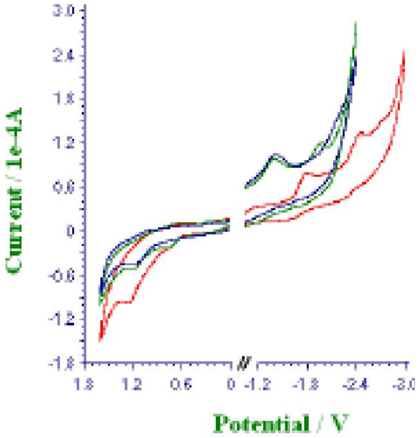


Figure 1 : CV curves of 5×10^{-3}mol/L PQSe (red line), PQS(green line) and PQ(blue line) in DMF+0.1M TBAP with scan rates 0.1V/s

The electrochemistry behavior of the six polymers is investigated by Cyclic Voltammetry (CV) in DMF +0.1 mol/L TBAP. Figure 1 shows the different redox processes of PQ, PQS and PQSe occurring at different potentials. The results indicate that PQ has a well-defined oxidative peak at 1.142V and a stable reductive peak at –1.401V. However, PQS has another oxidative peak at 1.196V and reductive peak at –1.974V besides the oxidative peak at 0.770V and the reductive peak at –1.385V. Although PQSe has also two pair redox peaks which are similar with that of PQS, the peak potentials are obviously different from that of PQS. The electrochemistry behavior of the other three polymers is semblable to that of PQS. The six polymers are structural analogs; therefore it is possible that they have similar redox behaviors. The datum of CV are listed in TABLE 1.

The redox peak separation value of the selenium-containing polymer is more positive than that of other without-selenium polymers. This can be attributed to

TABLE 1 : Electrochemical datum of the six polymers

Polymers	E_{pa}		E_{pc}	
PQ	--	1.184	-1.401	--
PQDB	0.780	1.186	-1.497	-2.041
PQDN	0.759	1.161	-1.478	-2.082
PQTN	0.739	1.183	-1.385	-1.968
PQS	0.764	1.196	-1.422	-1.818
PQSe	0.743	1.209	-1.794	-2.435

the electronegative selenium atom, which is bonded directly to the heterocyclic ring, causing the oxidation to be more difficult than that of other without-selenium polymers. At the same time, these results mean that the reduction of PQSe becomes more difficult when the S atoms on heterocyclic are substituted by electrophobic Se. It can be speculated that the electronic cloud is dispersed with the increase in electron-withdrawing ability of the substituents. The decrease of the electronic cloud density in the middle part of the molecule makes it difficult to lose electrons and ease to gain them, so as to raise the oxidative potential and reduce the reductive potential.

In addition, it was found that the peak current of the six polymers increased and the peak potential shifted to more positive values (oxidation peaks) or negative values (reductive peaks) with increasing scan rate and the I_{pa} and I_{pc} were linearly proportional to $v^{1/2}$, confirming the irreversible diffusion-controlled process for the six polymers electrochemical system. So the electron transfer number (n) was calculated using curve equation of normal pulse voltammetry (NPV):

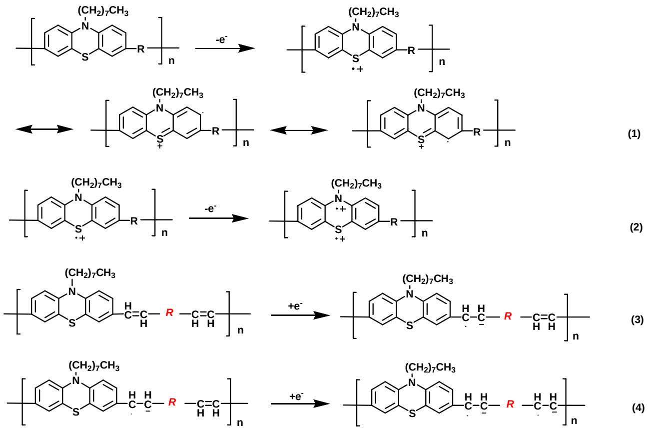
$$E = E_{1/2} + 2.303\frac{RT}{nF}\lg\frac{i_l - i}{i} \qquad (1)$$

Where E and $E_{1/2}$ are separately the potential and the half wave potential(V); n is the number of electron transferred, i represents the electrical current (A); and i_l expresses the limited electrical current (A). At 25 °C, the RT value becomes 2480 J·mol^{-1} and the Faraday constant is F=96487 C·mol^{-1}.

The results show that the six polymers are both one-electron redox processes. It is agreement with the results which the literature reported the other similar polymers previously[26, 27].

Based on the literature[28], the oxidation peaks were caused by the phenothiazine group of the polymers according to the reaction (1) and (2) in Scheme 2. There is only one electron transfer in the reaction process owing to the neutral molecule of the polymers in non-aqueous medium. This is different from the literature[28]. Also, for the other five polymers except PQ, there are strong electron donating group, thus the electronic cloud density is large, so they can continue to lose another electron when the potential shifted to more positive values, which is corresponding to the reaction (2).

In addition, based on the literature[26], the reductive peak was caused by vinyl group according to the reaction (3) in Scheme 2. Also, for the five polymers except PQ, there is strong electron donating group, therefore, they continued to gain another electron when the potential shifted to more negative values, which was corresponding to reaction (4). At the same time, the polymer is changed a twin-electron species. The possible electrode reaction mechanisms of the six polymers are shown in Scheme 2.



Scheme 2 : The possible electrode reaction mechanism of the six polymers.

Determination of the diffusion coefficient (D) and electrochemical reaction rate constant (k_s)

The diffusion coefficient (D) was calculated using the following electrochemical equation[29]:

$$i_p = 3.01\times10^5 n(n_\alpha \alpha)^{1/2} A D^{1/2} c v^{1/2} \qquad (2)$$

Where i_p is the peak current of the CV peak (A); A denotes the electrode surface area (cm^2); c represents the analyte concentration (mol·cm^{-3}), and the diffusion coefficient, D, in units of cm^2·s^{-1} can be determined from Eq. (2).

In addition, the potential step chronoamperometry (CA) and chronocoulometry (CC) method are widely used for the determination of the diffusion coefficients in diffusion controlled electrode processes based on the theoretical derivation presented initially by Wen et al.[30]. In this study, the potential steps from 0.8V to 1.4V were inflicted on the electrode and maintained for 1s. According to the Cottrell relationships[29] (Eq. (3)), and using the values of slope of Cottrell i-t$^{-1/2}$ and Q - t $^{1/2}$ plots, the diffusion coefficient D can be calculated.

$$\mathbf{i(t)=\frac{nFAD^{1/2}c}{(\pi t)^{1/2}}+i_{c}}$$

$$\mathbf{Q(t)=\frac{2nFAD^{1/2}ctg^{1/2}}{\pi^{1/2}}+Qdl} \qquad (3)$$

Where *t* is the elapsed time from the beginning of the step (s), and other parameters have either been discussed above or have their usual significance.

The D values of six polymers calculated are summarized in TABLE 2.

TABLE.2 : Electrochemical kinetics data of the six polymers

Polymer	D×10^6/(cm^2/s)			k_s×10^4/(cm/s)
	CA	CC	CV	
PQ	2.616	2.744	2.505	3.355
PQDB	1.419	1.302	1.295	2.128
PQN	1.132	1.232	1.112	1.817
PQTN	0.998	1.038	0.977	1.490
PQS	1.946	2.093	1.825	2.544
PQSe	1.277	1.308	1.250	2.020

The resulting values of diffusion coefficient obtained by the three methods are almost agreements. In addition, we can find the order of the D values: PQ> PQS> PQDB> PQSe> PQDN> PQTN, which agree with this concept of that D usually decreases with the increase of the molecular weight and the size of a molecule.

According to the relationship between peak potential (E_p) and scan rate (õ) of irreversible redox process (Eq. (4)):

$$\mathbf{E_{p}=E_{i}-\frac{RT}{\alpha nF}(0.780+0.51}$$

$$\mathbf{In\frac{\alpha n_{\alpha}DFv}{RT}-Ink_{s})} \qquad (4)$$

Where α is the transfer coefficients; *v* expresses scan rate (V·s^{-1}), and E_i and E_p are the standard peak potential and peak potential, separately. The electrochemical reaction rate constant k_s values (TABLE 2) can be calculated with the intercept of E_p ▪ ‘lnυ.

The results reveal that electrochemical reaction rate constant (k_s) of PQ is the largest in the six polymers. This is agreement with the phenomenon of diffusion coefficient (D).

The evaluation of the energy level (HOMO and LUMO)

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are two energy parameters that establish the positions of the frontier orbital. Extensive previous studies have illustrated that the energy parameters HOMO and LUMO are related to the measured redox onset potentials. In this work, the HOMO and LUMO levels of the six polymers were calculated with formula of E_{HOMO}= -|$E_{ox-onset}$+4.74| eV and E_{LUMO}= -|$E_{red-onset}$+4.74| eV[31, 32], where $E_{red-onset}$ and E_{ox-set} are respectively the onset reductive potential and the onset oxidative potential in volts versus the SCE. The energy gap E_g is the separation between the HOMO and LUMO level, thus E_g = E_{LUMO}–$E_{HOMO.}$ All the results are listed in TABLE 3.

TABLE 3 : The energy levels of the six polymers

Polymer	$E_{ox-onset}$ (V)	$E_{red-onset}$ (V)	HOMO (eV)	LUMO (eV)	E_g (eV)
PQ	0.953	-1.192	-5.693	-3.548	2.145
PQDB	0.596	-1.246	-5.336	-3.494	1.842
PQDN	0.633	-1.240	-5.373	-3.5	1.873
PQTN	0.609	-1.180	-5.349	-3.56	1.789
PQS	0.617	-1.219	-5.357	-3.521	1.836
PQSe	0.596	-1.584	-5.336	-3.156	2.18

The phenomenon can be explained by showing that the better conjugated property of PQSe results in the better charge-transporting property and the HOMO value of PQSe is higher than that of other polymers, with the result that hole injection into the HOMO level of PQSe from Fermi energy level is easier. The band gap of the PQSe is larger than that of the other polymers, which may also be aroused from the effect of the electronegative selenium atom. It is not surprising that the HOMO filled orbital in PQ is the lowest in all polymers, where no substituent at the phenothiazine reduce its HOMO level.

The effect of the polymers and metal ions

The voltammograms of free polymers, Zn^{2+} and Hg^{2+} complexed polymers in potential window of 0.4~1.6V are illustrated in Figure 2. As can be seen from Figure 2, the new well defined irreversible anodic waves in potential 0.6V (versus SCE), can be assigned to oxidation process of HgII/HgI. There are no oxidation peak of ZnII/Zn is detected in the range of the scan potentials. Compared with the free polymers, the addition of metal ions have shifted the oxidation peak potential of the corresponding phenothiazine group to more cathodal position (see TABLE 4 and the cyclic voltammograms of Figure 2). It is interesting to note that the first oxidation peak potential is nearly not changed, but the second oxidation peak potential is removed a lot. The reason may be that the reaction of metal ions and phenothiazine moieties. The phenomena help us to gain further insight into the reaction mechanism which is described above. The □E_{pa} values represent the difference between the potentials of in the Zn^{2+} or Hg^{2+} complexed ($E_{pa,c}$) and free ($E_{pa,f}$) polymers (TABLE 4). For those containing smaller sizes such as PQDN and PQSe, the bigger shift (178, 164 mV and 167, 139 mV, respectively) of oxidation potentials resulted from the addition of the Zn^{2+} and Hg^{2+} ions, respectively. On the other hand, for those with bigger sizes such as PQ and PQDB, the smaller shifts (70, 31 mV and 93, 55 mV, respectively) were obtained upon addition of Zn^{2+} and Hg^{2+} ions. It may be that the metal ionic radii and the coordination configuration of the polymers have an effect on the electrostatic repulsion through space between the polymers and the respective metal ions, and the stronger the repulsion that exists between them, the bigger peak potential shift is occured. It may be associated with the following aspects: (i) the size of the polymers; (ii) the ionic radii of the two metal ions in oxidation states; (iii) the coordination configuration, which depends on the ligand-field strength and the electronic states of the metal cations.

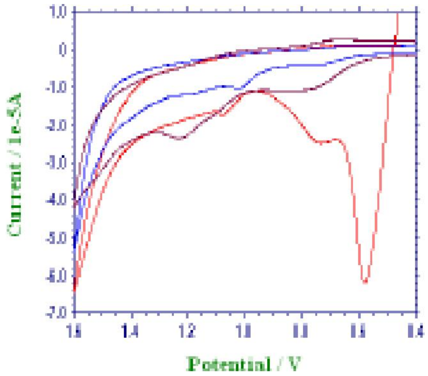


Figure 2 : CV curves of the free PQSe (brown line), Zn^{2+} complexed PQSe (blue line) and Hg^{2+} complexed PQSe (red line) in molar ratios of 1:1 with scan rates 0.1V/s

TABLE 4 : The peak potentials of free polymers and Zn^{2+} or Hg^{2+} complexed polymers

Polymers	$E_{pa\text{-}free}$ (V)	$E_{Poly\text{-}Zn^{2+}}$ (V)	$\Delta E_{pa\text{-}Zn^{2+}}$ (V)	$E_{Poly\text{-}Hg^{2+}}$ (V)	$\Delta E_{pa\text{-}Hg^{2+}}$ (V)
PQ	1.184	1.114	0.07	1.153	0.031
PQDB	1.186	1.093	0.093	1.131	0.055
PQDN	1.161	0.983	0.178	0.997	0.164
PQTN	1.183	1.081	0.102	1.151	0.032
PQS	1.196	1.087	0.109	1.108	0.088
PQSe	1.209	1.042	0.167	1.079	0.13

In addition, It is not surprised that the □E_{pa} is increased gradually as the concentration of metal cations increased in different molar ratios of 1:1, 1:2, 1:3. It may be that every polymer has several monomers, and the metal cations can react with only part of monomers.

CONCLUSIONS

In this paper, the electrochemical property of the six novel conjugated conducting polymers was investigated in detail. Every polymer except PQ has two oxidative peaks and two reductive peaks in potential –2.4~1.6V. The peak potential of PQSe is obviously different from that of other polymers. This can be attributed to the electronegative selenium atom, which is bonded directly to the heterocyclic ring, causing the oxidation to be more difficult than that of other without-selenium polymers. The research on the electrochemical effect of the polymers and metal ions show that the addition of metal ions had shifted the oxidation peak potential of the corresponding phenothiazine group to more cathodal position. The phenomena help us to gain further insight into the reaction mechanism which is described above.

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