高等学校化学学报
CHEMICAL JOURNAL OF CHINESE UNIVERSITIES
研究论文

二甲氧基取代的环戊联噻吩共轭聚合物的电致变色性能与稳定性

唐一潇[1,2], 王博涵[2], 夏思琪[1], 董玉杰[1], 李维军[1], 马於光[2]
(1. 浙江工业大学化学工程学院, 绿色化学合成与转化技术全国重点实验室, 杭州 310014;
2. 华南理工大学材料科学与工程学院, 发光材料与器件全国重点实验室, 广州 510640)

摘要 环戊联噻吩(CPDT)类聚合物因其良好的色彩可调性, 成为多色电致变色材料的潜在研究平台. 然而, 循环稳定性不足的问题限制了其实际应用的推进. 本文设计合成了2种不同取代基的CPDT共轭聚合物: PCPDT-Ph(以无取代苯环为共聚单元)和PCPDT-PhOMe(以二甲氧基取代苯环为共聚单元), 探究了二甲氧基取代对聚合物电致变色性能与稳定性的影响. 电化学与电致变色性能测结果表明, 二甲氧基的给电子效应实现了聚合物性能的有效调控, 并改善了循环稳定性. 与PCPDT-Ph相比, PCPDT-PhOMe的电化学起始氧化电位由0.66 V(*vs*. Ag/AgCl)降低至0.46 V, 最高占据分子轨道(HOMO)能级上移, 理论计算光学带隙由1.73 eV减小至1.61 eV. PCPDT-PhOMe薄膜在中性态呈现品红色, 氧化态则为透明, 色差值(ΔE^*_{ab})达46.36; 着色/褪色响应速度为0.7/0.6 s, 经1000次循环后光学对比度保留率达84%, 优于PCPDT-Ph薄膜(500次循环后对比度保留率为79.5%), 且着色效率为543.9 cm^2/C, 展现出良好的电致变色综合性能. 基于PCPDT-PhOMe组装的电致变色器件可实现品红至透明的可逆切换, 响应时间不大于1.0 s, 且经30000次循环后对比度保留率仍达71%, 稳定性良好. 研究结果揭示了取代基电子效应在CPDT类聚合物电致变色性能调控中的作用, 为可溶液加工的噻吩类电致变色材料的分子设计提供了理论支撑与实验依据, 同时证实了PCPDT-PhOMe在智能窗、电子显示等领域的潜在应用价值.

关键词 二甲氧基取代; 环戊联噻吩; 电致变色器件
中图分类号 O631 **文献标志码** A doi: 10.7503/cjcu20250323

Electrochromic Properties and Stability of Dimethoxy-substituted Cyclopentadithiophene-based Conjugated Polymers

TANG Yixiao[1,2], WANG Bohan[2], XIA Siqi[1], DONG Yujie[1],
LI Weijun[1*], MA Yuguang[2*]
(*1. State Key Laboratory of Green Chemical Synthesis and Conversion, College of Chemical Engineering, Zhejiang University of Technology, Hangzhou* 310014, *China*;
2. State Key Laboratory of Luminescent Materials and Devices, College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, *China*)

Abstract Cyclopentadithiophene(CPDT)-based polymers have emerged as promising research platforms for multi-color electrochromic materials due to their favorable color tunability. However, insufficient cyclic stability has hindered their translation into practical applications. In this study, two CPDT-based conjugated polymers with

收稿日期: 2025-10-31. 网络首发日期: 2025-12-06.
联系人简介: 李维军, 男, 博士, 副教授, 主要从事有机光电功能材料与器件方面的研究. E-mail: liwj@zjut.edu.cn
马於光, 男, 博士, 教授, 主要从事有机光电功能材料与器件方面的研究. E-mail: ygma@scut.edu.cn
基金项目: 国家自然科学基金(批准号: 52103232)和浙江省自然科学基金(批准号: LY24E030012, LY19E030006)资助.
Supported by the National Natural Science Foundation of China(No.52103232) and the Natural Science Foundation of Zhejiang Province, China (Nos.LY24E030012, LY19E030006).

distinct substituent groups were designed and synthesized: PCPDT-Ph (copolymerized with unsubstituted benzene units) and PCPDT-PhOMe (copolymerized with dimethoxy-substituted benzene units). The influence of dimethoxy substitution on the electrochromic properties and stability of the polymers was systematically investigated. Electrochemical and electrochromic characterizations demonstrated that the electron-donating ability of the dimethoxy groups not only effectively regulated the polymer's intrinsic properties but also significantly enhanced its cycling stability. Compared with PCPDT-Ph, PCPDT-PhOMe exhibited a reduced onset oxidation potential from 0.66 V (*vs.* Ag/AgCl) to 0.46 V, an upshifted highest occupied molecular orbital (HOMO) energy level, and a narrowed optical band gap (calculated theoretically) from 1.73 eV to 1.61 eV. The PCPDT-PhOMe film showed magenta in the neutral state and transparency in the oxidized state, with a color difference (ΔE^*_{ab}) of 46.36. The coloring/bleaching response times were measured as 0.7/0.6 s, and the optical contrast retention reached 84% after 1000 cycles, outperforming the PCPDT-Ph film (79.5% retention after 500 cycles). Additionally, it exhibited a coloration efficiency of 543.9 cm^2/C, demonstrating favorable comprehensive electrochromic performance. Electrochromic devices assembled with PCPDT-PhOMe achieved reversible switching between magenta and transparent states, with a response time of ≤1.0 s and a contrast retention of 71% after 30000 cycles, indicating good stability. This work clarifies the role of substituent electronic effects in regulating the electrochromic properties of CPDT-based polymers, providing experimental basis and theoretical support for the molecular design of solution-processable thiophene-based electrochromic materials. Furthermore, it validates the potential application of PCPDT-PhOMe in smart windows, electronic displays, and other related fields.

Keywords Dimethoxy-substitution; Cyclopentadithiophene; Electrochromic device

1 Introduction

Electrochromic materials (ECM) achieve reversible color changes through the regulation of external potential and hold tremendous commercial potential in fields such as intelligent displays[1,2], energy-saving buildings[3,4], and flexible electronics[5,6]. Solution-processed conjugated polymers have been widely studied and applied in practical scenarios due to their excellent processability, facile large-scale production, flexible color tunability, and rapid response kinetics[7~10]. Colored-to-transparent switching conjugated polymers can achieve full visible light transmission in the oxidized state, thus exhibiting high contrast and being suitable for applications demanding high resolution[11]. Notably, the conjugated polymer system based on thiophene derivatives, pioneered by Reynolds and his collaborators[12~16], has evolved into a relatively mature multicolor electrochromic platform. However, some of these materials suffer from poor cycle stability and low coloring efficiency, which hinder their long-term application in practical devices.

Beyond traditional monomers such as thiophene, 3,4-ethylenedioxythiophene (EDOT), and thieno[3,2-*b*]thiophene (TT), cyclopentadithiophene (CPDT) is also a typical electron donor unit. Its rigid conjugated structure can not only effectively extend the π-conjugated system of the polymer main chain and improve carrier mobility but also regulate the molecular energy gap by combining with different electron acceptors or neutral units[17,18], thus affording an ideal structural scaffold for the optimization of electrochromic properties. In 2007, it was reported that polycyclopentadithiophene (PCPDT) exhibited low absorption in the oxidized state and excellent electrochromic properties, enabling switching from blue-violet to high transmittance[19]. This work verified the feasibility of CPDT-based colored-to-transparent materials, but the regulatory effect of substituent modification on their optical and electrochemical properties remains underexplored. In particular, the introduction of copolymer units such as phenyl rings can modulate the electron cloud distribution of the conjugated system through the modification of substituents (electron-donating or electron-withdrawing), thereby affecting the optical and electrochemical properties of the material.

Based on this, two conjugated polymers, PCPDT-Ph (unsubstituted benzene ring) and PCPDT-PhOMe (dimethoxy-substituted benzene ring), with CPDT as the electron donor and different substituted benzene rings as copolymer units were designed and synthesized herein. Finally, an electrochromic device was assembled based on PCPDT-PhOMe with better performance to verify its practical application potential. This study aims to clarify the structure-property relationship of CPDT-based polymers modified by distinct substituent groups, expand the family of soluble colored-to-transparent electrochromic polymers, and provide a theoretical and experimental basis for the precise design of high-performance electrochromic materials.

2 Experimental

2.1 Materials and Measurements

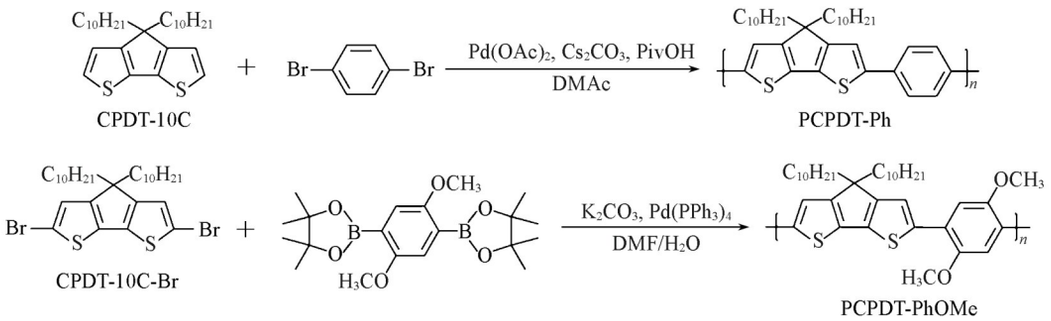
All chemicals used were commercial products and were used as received, without further purification. 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene, 1-bromodecane, tetrabutylammonium iodide, sodium hydroxide, *N*-bromosuccinimide (NBS), anhydrous potassium carbonate, tetrakis (triphenylphosphine) palladium ($Pd[P(C_6H_5)_3]_4$), anhydrous cesium carbonate, 1,4-dibromobenzene, palladium acetate, pivalic acid, *N*,*N*-dimethylformamide (DMF), *N*, *N*-dimethylacetamide (DMAc), tetrabutylammonium hexafluorophosphate ($TBAPF_6$), acetonitrile (ACN) were purchased from Aladdin. 2,2′-(2,5-dimethoxy-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) was purchased from Adamas. Anhydrous sodium sulfate, sodium chloride, anhydrous ethanol, petroleum ether (boiling range 60—90 ℃), dichloromethane, ethyl alcohol, chloroform, acetone were purchased from Hangzhou Huadong Pharmaceutical Co. Indium tin oxide (ITO) glass substrates (CSG HOLDING Co., Ltd., R_s≤10 Ω^{-1}, size: 0.9 cm/2.5 cm×4 cm) were purchased from Liaoning Huite Photoelectric Technology, Ltd.. The ITO glasses were cleaned sequentially in aqueous sodium hydroxide (0.5%, mass fraction), deionized water, ethanol, toluene, and acetone with ultrasonic treatment for 30 min before using, and finally they were soaked in clean acetone for spare use.

The ^{1}H NMR (400 MHz) spectra of all these synthesized monomers and polymers were recorded by using the Bruker AVANCE III instrument (Bruker, Switzerland) with $CDCl_3$ as the solvent and TMS as the internal standard. The average molecular weights and polydispersity indices (PDIs) were measured by gel permeation chromatography (GPC; Waters GPC 1515). The polymer films were prepared by spin coater (WS-650MZ-23NPPB, MYCRO, China). FTIR spectroscopy was measured by a Nicolet 6700 spectrometer (Thermo Fisher Nicolet). These electrochemical properties of the polymer films were measured by CHI 660E electrochemical analyzer (Chen Hua, China). Electrochemical measurements were performed in a three-electrode cell with an ITO glass coated with polymer film as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl in saturated KCl solution as the reference electrode. The spectroelectrochemical and kinetic properties of films were investigated by the Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan) combined with the CHI 660E electrochemical analyzer. The color coordinate data were obtained by CM-3600d spectrophotometer (Konica Minolta, Japan) combined with CHI 660E electrochemical analyzer in the International Commission on Illumination CIE 1976 *L***a***b** Color Space. The thickness of the films was measured by a step profiler (Bruker, Switzerland).

2.2 Synthesis of Polymers

The 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (CPDT) was alkylated according to the literature[20]. The product of partial alkylation was brominated with NBS. Under the action of palladium catalyst, the target monomers were subjected to Suzuki polymerization and direct arylation polycondensation (Scheme 1). The detailed synthesis procedures, as well as relevant ^{1}H NMR spectra, polymer molecular weights, FTIR

spectra, and other related data are provided in Scheme S1 and Figs. S1—S5(see the Supporting Information of this paper).



Scheme 1 Syntheses of PCPDT-Ph and PCPDT-PhOMe

2.3 Preparation of Electrochromic Films

Preparation of spin-coated films: the polymer was dissolved in trichloromethane and ultrasonicated for 5 min to obtain a 10 mg/mL polymer solution. The polymer solution was filtered by Nylon 66 filter(pore size 22 μm), then the solution was spin-coated on the conductive surface of ITO glass(size 0.9 cm×4 cm). After the spinning process, the films were naturally dried in the air to obtain electrochromic films. The thickness of the PCPDT-Ph and PCPDT-PhOMe films were measured to be about 94 and 91 nm, respectively(Fig. S6, see the Supporting Information of this paper).

Preparation of the sprayed films: 6 mg/mL polymer chloroform solution was prepared by the above method. The polymer solution was evenly sprayed on the surface of ITO glass(size 2.5 cm×4 cm), and the spraying time was controlled to obtain the appropriate film thickness. After the spraying, they were dried in the air to obtain the electrochromic films.

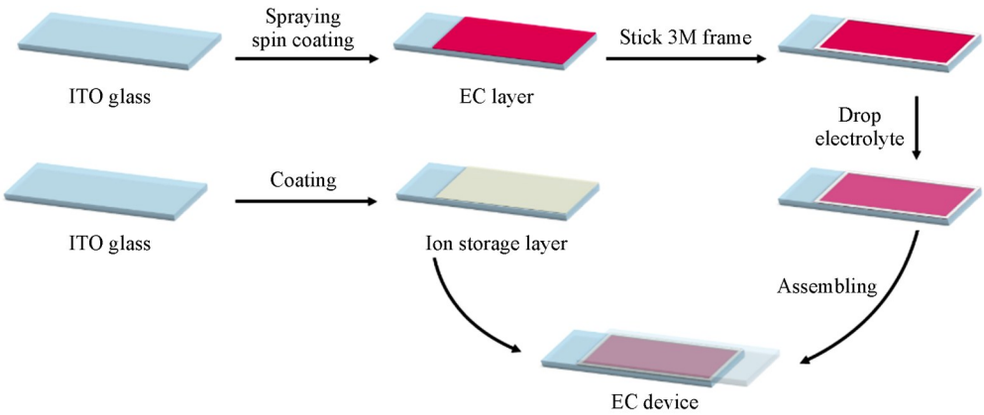
The spin-coated films were used for performance testing, and the sprayed films were used for device assembly.

2.4 Fabrication of Electrochromic Devices

2.4.1 Preparation of Gel Electrolyte 6.00 g polymethyl methacrylate (PMMA) and 24.00 g propylene carbonate were added to a clean sample bottle. The sample bottle was sealed and placed in an oven at 60 ℃ for about one week. After the mixture was in a uniform gel state, two electrolytes of 3.48 g 1-*n*-butyl-3-methylimidazolium trifluoromethanesulfonate and 0.81 g lithium tetrafluoroborate were added to the sample bottle, then 12.00 g chromatographic grade acetonitrile and 12.00 g chromatographic grade dichloromethane were added. The electrolyte was completely dissolved in the gel by ultrasound, and the excess solvent was removed by rotary evaporation to finally obtain the gel electrolyte.

2.4.2 Preparation of Ion Storage Solution The mixture of polymethyl methacrylate and propylene carbonate was swelled according to the above ratio and method. After the swelling was completed, 3.48 g 1-*n*-butyl-3-methylimidazolium trifluoromethanesulfonate and 0.68 g hydroquinone were added to the sample bottle[21], then 24.00 g chromatographic grade acetonitrile was added. The electrolyte was completely dissolved in the gel by ultrasound to obtain an ion storage solution.

2.4.3 Assembly of the Devices A piece of washed ITO glass was taken, and the ion storage solution was evenly applied to the conductive surface, waiting for the film to dry naturally(Scheme 2). The 3M tape frame was pasted onto the ITO glass containing electrochromic film. After adding gel electrolyte, the ITO glass containing ion storage layer was covered. After assembly, the excess electrolyte on the surface of the device was wiped off, and the electrochromic device was obtained by natural air drying. Excluding the 3M adhesive frame area, the actual working area of the electrochromic device is 2.1 cm×2.1 cm×0.3 mm.



Scheme 2　Assembly diagram of the EC device

3　Results and Discussion

3.1　Photophysical and Electrochemical Properties

In order to clarify the relationship between the color, optical absorption, redox potential and molecular structure of these two polymers, the simulated energy level calculation test, UV-Vis absorption spectra test and electrochemical test were carried out on the polymers. Theoretical calculations were performed on the molecular structures of polymer dimers using the Dmol3 module of Material Studio. For the calculated structures, structure optimization was conducted with the hybrid density functional theory (DFT) functional under the B3LYP/6-31G(*d*) basis set. Additionally, theoretical calculations on the frontier molecular orbitals of the molecules were carried out.

Fig.1 shows the orbital energy and energy gap of the following two polymer dimers simulated by Material

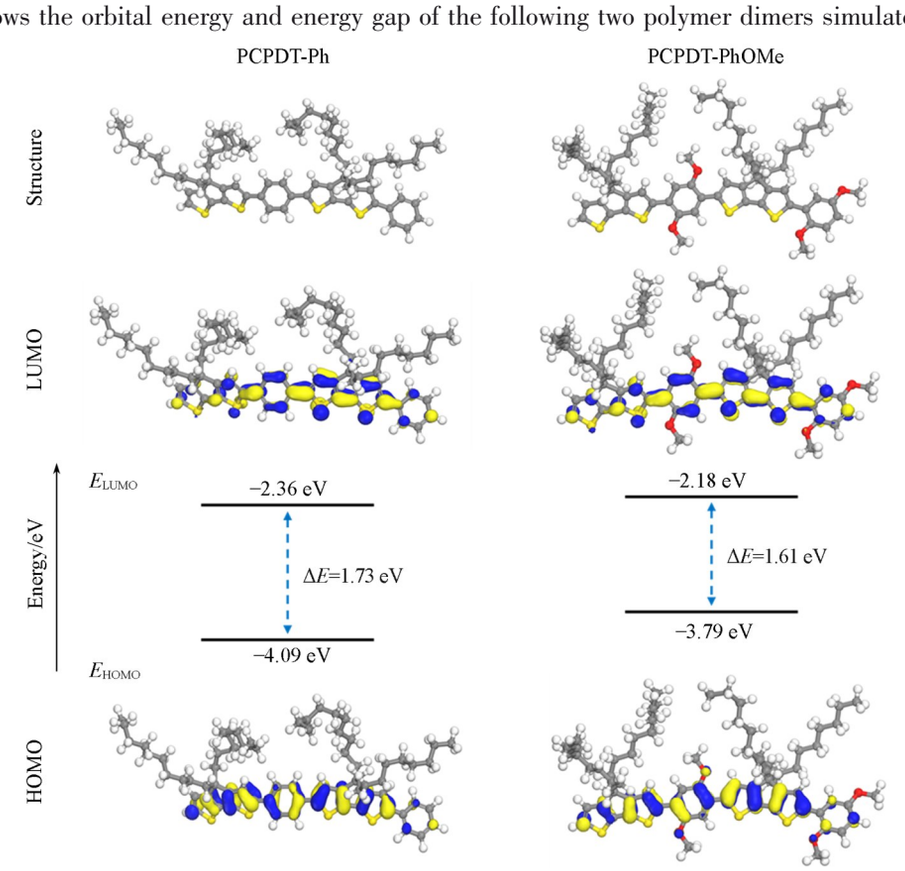


Fig. 1　Molecular orbitals and optical energy gaps of the dimeric structures of PCPDT-Ph and PCPDT-PhOMe

studio. It can be clearly seen that the highest occupied molecular orbital(HOMO) and the lowest unoccupied molecular orbital(LUMO) are mainly formed by the contribution of cyclopentadithiophene and benzene ring. Due to the p-π conjugation effect of methoxy groups, the electron cloud density of the benzene ring of PCPDT-PhOMe increases. The higher the electron cloud density, the easier electrons are excited, and the HOMO energy level undergoes a significant upshift. Moreover, the introduction of methoxy groups will make the electron distribution in the polymer more uniform, which reduce the weak intramolecular charge transfer(ICT) between cyclopentadithiophene and benzene rings, resulting in a slight increase in LUMO energy level. Since the increase of HOMO level is much larger than that of LUMO level(ΔHOMO>ΔLUMO), according to the formula E_g=LUMO−HOMO, the optical band gap of PCPDT-PhOMe(1.61 eV) is significantly narrower than that of PCPDT-Ph(1.73 eV).

UV-Vis absorption spectra of the films and solutions of the two polymers in the neutral state are shown in Fig.2(A). The solvent for the polymer solution was dichloromethane, and the polymer films were spin-coated on ITO glass electrodes. The spectra of the two materials in the solvent state are basically consistent with those in the aggregated state. Their absorption ranges are essentially identical, while the absorption peaks of the aggregated films are slightly broader than those of the solutions. Based on the UV-Vis spectra of the PCPDT-Ph and PCPDT-PhOMe films, their optical band gaps were calculated using the empirical formula: optical band gap $E_{g,opt}$/eV=1240/λ_{onset}(λ_{onset} is the onset absorption in film), with the results determined to be 2.03 and 2.01 eV, respectively. The comparison result of the optical band gaps of the two polymers obtained from the theoretical calculation is also consistent with that *via* the experiment.

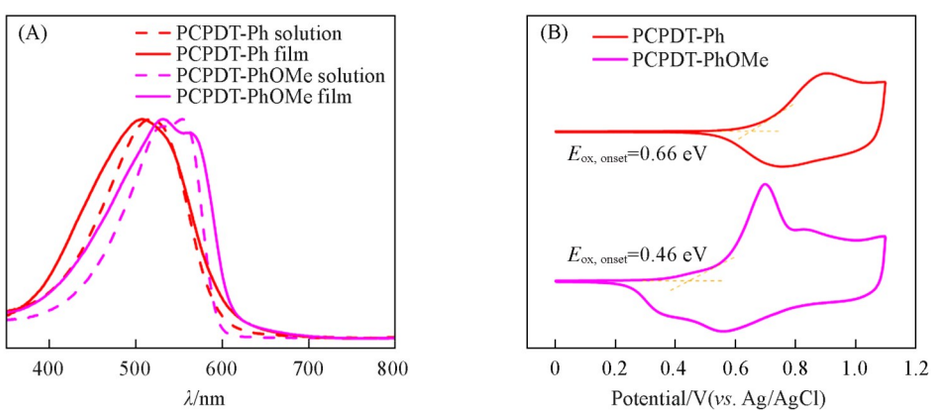


Fig. 2 Normalized UV-Vis absorption spectra of PCPDT-Ph and PCPDT-PhOMe in films(in the neutral state) and in chloroform solution(A), and the cyclic voltammograms of polymer films PCPDT-Ph and PCPDT-PhOMe at a scanning rate of 100 mV/s(B)

The electrochemical test was carried out with ITO electrode coated with polymer film as working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode. Fig.2(B) shows the CV curves of these two polymers at a scan rate of 100 mV/s in 0.1 mol/L TBAPF$_6$/ACN. These two polymers have relatively lower initial oxidation potentials($E_{ox,onset}$)(0.4—0.7 V *vs.* Ag/AgCl) due to the donor structure(CPDT) of the polymer backbone, which makes them easy to oxidize. The $E_{ox,onset}$ of PCPDT-PhOMe(0.46 V) is lower than that of PCPDT-Ph(0.66 V), this is attributed to the electron-donating methoxy group on the benzene ring of PCPDT-PhOMe. The distinct optical band gaps and electrochemical redox behaviors of the two polymers result in pronounced differences in their subsequently measured electrochromic properties. Table 1 summarizes the $E_{ox,onset}$, λ_{onset}, HOMO and LUMO energy levels, and optical energy band gap($E_{g,opt}$) values of two polymers, as well as the HOMO, LUMO energy levels and energy gap data for two polymer dimers calculated by the Materials Studio.

Table 1 Optical and electrochemical properties of PCPDT-Ph and PCPDT-PhOMe

Polymer	PCPDT-Ph	PCPDT-PhOMe
$E_{ox,onset}$/V	0.66	0.46
λ_{onset}/nm	610	616
$E^{a}_{g,opt}$/eV	2.03	2.01
LUMO^{b}/eV	−3.23	−3.05
HOMO^{b}/eV	−5.26	−5.06
LUMO^{c}/eV	−2.36	−2.18
HOMO^{c}/eV	−4.09	−3.79
E_g^{c}/eV	1.73	1.61

a. Optical band gap calculation: $E_{g,opt}$=1240/λ_{onset} (eV); *b*. energy level calculation: HOMO=−4.8 eV−$E_{ox,onset\,(vs.\ Ag/AgCl)}$ + $E_{Fc/Fc+(vs.\ Ag/AgCl)}$; LUMO=$E_{g,opt}$+HOMO; *c*. theoretical calculation values.

The cyclic voltammetry curves of PCPDT-Ph and PCPDT-PhOMe films recorded at various scan rates in 0.1 mol/L TBAPF$_6$/ACN are shown in Fig.3(A) and (B), to examine the scan rate dependence of the polymer films. As the scan rate increases from 30 mV/s to 300 mV/s, the oxidation peak gradually shifts toward more positive potentials, accompanied by an increase in peak current intensity. The relationship between peak current intensity and scan rate is shown in Fig.3(C) and (D). Linear fitting of the anodic and cathodic peak current densities versus the scan rate reveals that the redox process of the two polymers is non-diffusion controlled and well adhered to the electrode surface[22]. Consequently, even at high scan rate, the polymer film does not fall off the ITO electrode or diffuse into the electrolyte. During the redox process, the charge can diffuse into the polymer film, resulting in a stable electrochromic process of the polymer film.

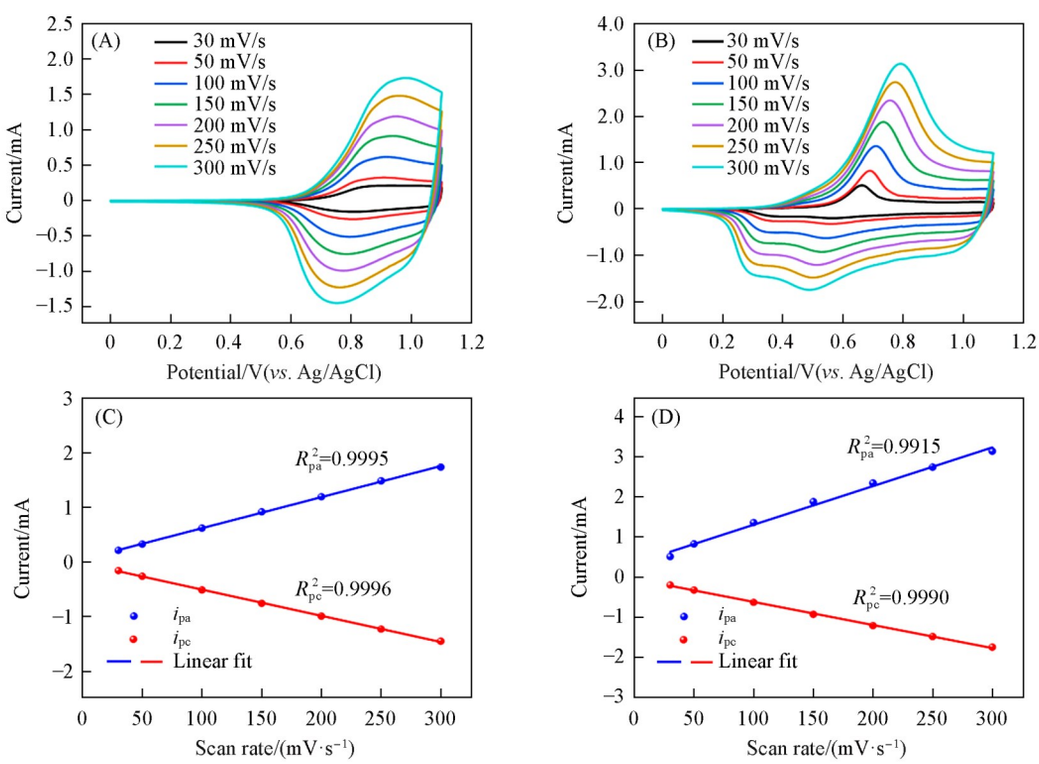


Fig. 3 Cyclic voltammograms of polymer films PCPDT-Ph(A) and PCPDT-PhOMe(B) at different scan rates and scan rate-peak current curves of PCPDT-Ph(C) and PCPDT-PhOMe(D)

3.2 Spectroelectrochemical Properties

The spectroelectrochemical test was carried out in the 0.1 mol/L TBAPF$_6$/ACN and a three-electrode system. In the process of electrochemical redox, the electronic structure of the polymer changes, which leads

to the change of spectrum absorption and color. Fig. 4(A) and (B) shows the change of UV-Vis spectra of the two polymers with the increase of potential. In the neutral state(0 V), PCPDT-Ph and PCPDT-PhOMe films have a clear absorption peak at 400—600 nm, which is attributed to the π-π^* transition absorption of the polymer skeleton. The positions of the maximum absorption peaks(λ_{max}) of PCPDT-Ph and PCPDT-PhOMe films are located at 507 nm and 532 nm respectively. With the increase of applied potential, the change trend of UV spectra of the two polymers is basically the same: the π-π^* transition absorption gradually weakens and disappears almost completely in the end, at the same time, the absorption in the near-infrared region of 780—1100 nm begins to increase, forming polarons and bipolarons[23,24]. At 1.1 V, the two polymer films are completely oxidized and have a high transmittance in the visible region.

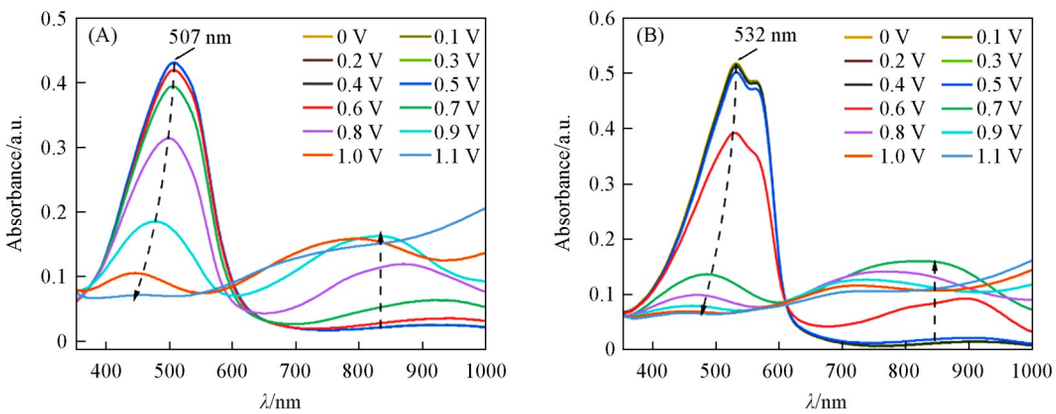


Fig. 4 UV absorption curves of the polymer films PCPDT-Ph(A) and PCPDT-PhOMe at different potentials(B)

According to the results of the colorimetric test in Fig.5(A) and (B), PCPDT-Ph film shows a red color (L^*=81.08, a^*=28.46, b^*=6.74) and PCPDT-PhOMe film shows a magenta color (L^*=71.45, a^*=36.61, b^*=−14.09) in the neutral state(0 V). When the applied potential gradually increases, the a^*b^* values of both polymer films gradually approach the origin (0,0), at the same time, the L^* values of the films gradually increase with the increase of the potential until the polymer films are completely oxidized and reaches the maximum values, both films change from colored to transparent.

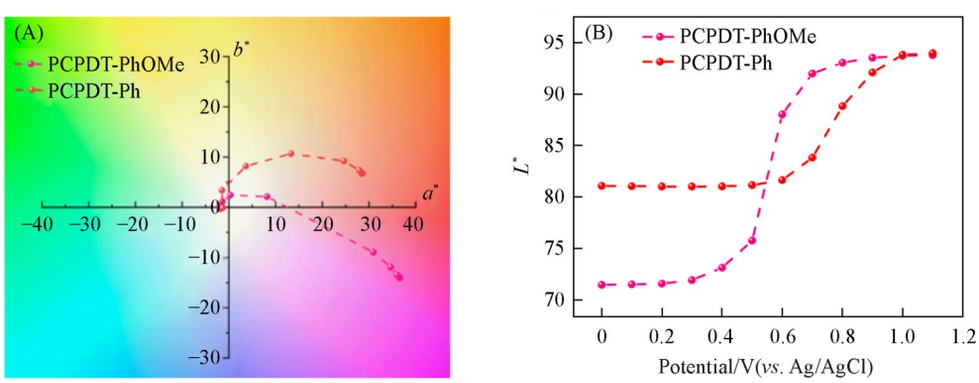


Fig. 5 a^*b^* (A) and L^* (B) values of the polymer films PCPDT-Ph and PCPDT-PhOMe at different potentials

To quantitatively evaluate the parameters, the chromatic color(C^*_{ab}) and color saturation(S^*_{ab}), they can be calculated by the following formula[25]:

$$C^*_{ab} = \sqrt{(a^*)^2 + (b^*)^2} \tag{1}$$

$$S_{ab}^{*}=\frac{C_{ab}^{*}}{\sqrt{C_{ab}^{*2}+L^{*2}}}\times 100\%=\frac{\sqrt{\left(a^{*}\right)^{2}+\left(b^{*}\right)^{2}}}{\sqrt{\left(a^{*}\right)^{2}+\left(b^{*}\right)^{2}+L^{*2}}}\times 100\% \tag{2}$$

In the formula: L^{*} is used to describe the lightness of the color; a^{*} is used to characterize the red-green bias of the color; b^{*} is employed to depict the yellow-blue bias of the color.

C_{ab}^{*} and S_{ab}^{*} can be used to quantify the transparency of the bleached state of polymer films. The low C_{ab}^{*} value indicates that the color of the polymer film is close to neutral gray or colorless state[26,27]. At this time, if the light transmittance is high, that is, the S_{ab}^{*} value is also small, it can be judged that the bleached state of the film is transparent. Specifically, when the films are completely oxidized (at 1.1 V), these C_{ab}^{*} values of PCPDT-Ph film and PCPDT-PhOMe film are 1.36 and 1.41, while the S_{ab}^{*} values of PCPDT-Ph film and PCPDT-PhOMe film are 1.44% and 1.50%, respectively. As a result, they are close to the true colorless transmissive state. Further, the color difference (ΔE_{ab}^{*}) in the films is characterized as the distance between points in the CIE $L^{*}a^{*}b^{*}$ color space, with the specific calculation method presented as follows:

$$\Delta E_{ab}^{*}=\sqrt{(L_{2}^{*}-L_{1}^{*})^{2}+(a_{2}^{*}-a_{1}^{*})^{2}+(b_{2}^{*}-b_{1}^{*})^{2}} \tag{3}$$

The color differences ΔE_{ab}^{*} of two polymer films in bleached and colored states were calculated. PCPDT-PhOMe film shows a larger ΔE_{ab}^{*} value of 46.36 compared with that of 33.20 for PCPDT-Ph film. This indicates that PCPDT-PhOMe material has greater optical modulation capability. Electrochromic materials with high color difference can provide core performance support in practical scenarios such as energy consumption reduction of smart windows and clarity improvement of electronic displays. The chromaticity properties of these two polymer films are summarized in Table 2.

Table 2 The chromaticity properties of polymer films PCPDT-Ph and PCPDT-PhOMe

	PCPDT-Ph		PCPDT-PhOMe	
	Neut.	Ox.	Neut.	Ox.
a^{*}	28.46	−1.35	36.61	−1.41
b^{*}	6.74	−0.14	−14.09	0.04
L^{*}	81.08	93.98	71.45	93.79
C_{ab}^{*}	29.25	1.36	39.23	1.41
S_{ab}^{*}	33.93%	1.44%	48.13%	1.50%
ΔE_{ab}^{*} #	33.20		46.36	

ΔE_{ab}^{*} is the color difference between neutral state and oxidation state.

3.3 Kinetic Properties of Polymer Films

The switching properties of polymer films were studied by chronoamperometry method. The step potentials were set to 0 and 1.1 V, and the time interval was 5 s. The films were repeatedly switched between the oxidation state and the neutral state, and the transmittance was measured at the maximum absorption of the neutral polymer. As shown in Fig.6 (A) and (B), the switching time of PCPDT-Ph film at 507 nm are 0.8 s/0.3 s, and PCPDT-PhOMe film at 532 nm are 0.7 s/0.6 s. Owing to the incorporation of the cyclopentadithiophene (CPDT) unit, its intrinsically rigid molecular configuration facilitates the extension of the polymer's conjugated backbone, which is conducive to enhancing carrier mobility. Moreover, the introduction of CPDT significantly narrows the band gap of the polymer, thereby endowing the copolymer with a favorable foundation for charge transport. Since improved charge transport efficiency can reduce the time consumed by carrier migration, both polymer films exhibit a remarkably accelerated response speed. At the same time, it can be concluded that the contrasts of PCPDT-Ph film and PCPDT-PhOMe film at λ_{max} (507 nm and 532 nm) are 47.3% and 56.4%, respectively. PCPDT-PhOMe film has a larger contrast at the same film thickness, this result corresponds to the above colored and bleached ΔE_{ab}^{*} of two films.

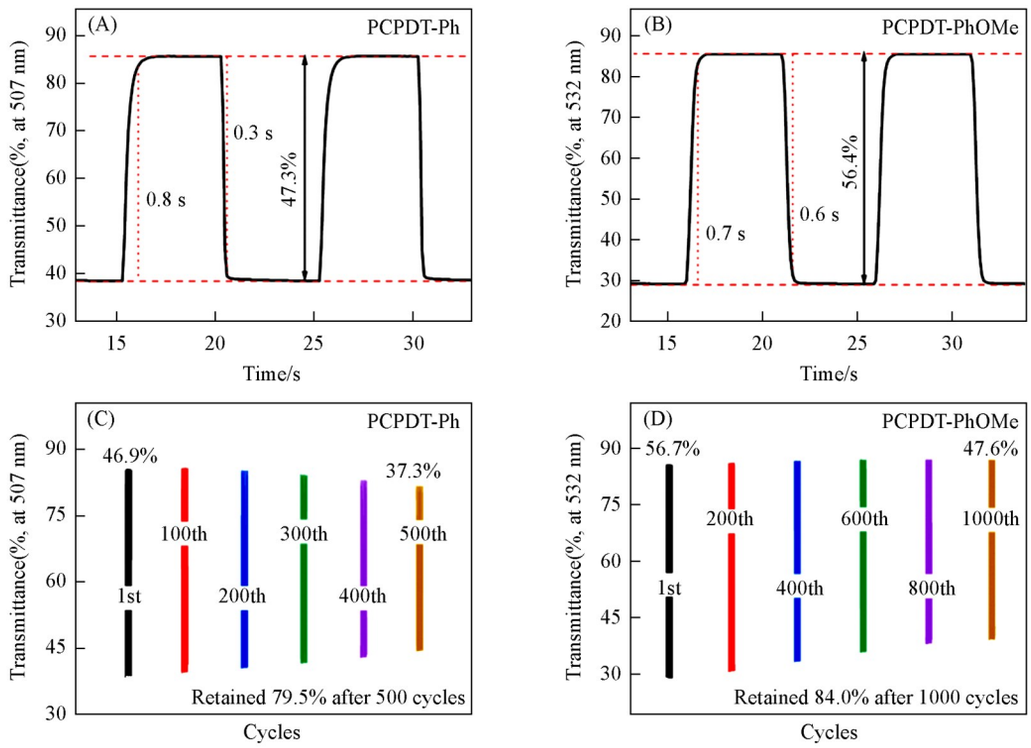


Fig. 6 Optical contrast and response time(A, B) and cyclic stability(C, D) of PCPDT-Ph(A, C) and PCPDT-PhOMe(B, D) polymer films at λ_{max}

The cycle stability of electrochromism is an important factor to determine whether the electrochromic technology can achieve commercial application. It can be observed that PCPDT-Ph film retains 79.5% of optical contrast(from 46.9% to 37.3%) after 500 cycles[Fig. 6(C)], and PCPDT-PhOMe film retains 84% of optical contrast(from 56.7% to 47.6%) after 1000 cycles[Fig. 6(D)]. During the cycling process, the transmittance of the bleached state is basically unchanged, while the transmittance of the colored state gradually increases, which leads to a decrease in the case of PCPDT-PhOMe film. In contrast, the transmittance of the bleached PCPDT-Ph film decreases also continuously during the test, which leads to the stability of the PCPDT-Ph film is not as good as that of the PCPDT-PhOMe film. According to the literature, the reasons for the decrease of the stability of thiophene polymers might be the irreversible capture of electrolyte ions, the relaxation of polymer molecular structure and the peroxidation of thiophene groups[28].

Coloring efficiency(CE) stands as a pivotal performance parameter for electrochromic materials, and it is typically determined *via* the following equation:

$$CE(\lambda) = \frac{\Delta OD}{Q_d} = \frac{\lg(\frac{T_{ox}}{T_{neut}})}{\frac{Q}{s}} \tag{4}$$

In the formula: ΔOD(optical density change) denotes the variation in optical density at a specific wavelength, which is calculated from the transmittance values of the oxidized state (T_{ox}) and the neutral state (T_{neut}); Q_d represents the charge density injected into or extracted from per unit area. It is obtained by dividing the total injected/extracted charge(Q) by the effective electrochromic area(s).

According to the calculation formula, as shown in Fig.7(A) and (B), the coloring efficiencies of PCPDT-Ph film and PCPDT-PhOMe film are 567.7 and 543.9 cm^2/C. Both films show relatively high coloration efficiency at a thinner film thickness(<100 nm) compared to the thiophene polymers reported in the literature[29~33]. The

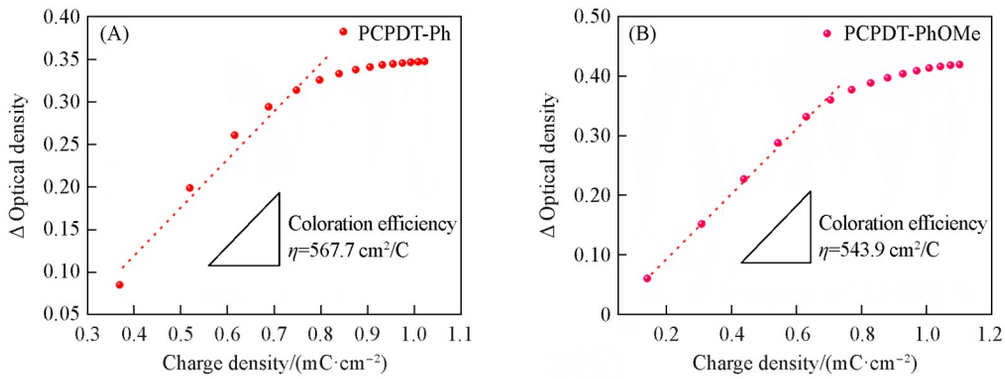


Fig. 7 Coloration efficiency of the polymer films PCPDT-Ph(A) and PCPDT-PhOMe(B) at λ_{max}

relatively high coloration efficiency of the polymer is beneficial to achieve more significant optical contrast switching and more energy saving in electrochromic devices with lower driving voltage and energy consumption. The coloration efficiencies of different thiophene polymers have been summarized in Table 3.

Table 3 Comparison of coloration efficiency among different thiophene polymers

Polymer	λ_{max}/nm	CE/(cm²·C⁻¹)	Ref.	Polymer	λ_{max}/nm	CE/(cm²·C⁻¹)	Ref.
PBBrPOT	556	111	[29]	P(F-EDOT)	458	192	[32]
PEDOT	585	137	[30]	P1	450	38	[33]
PProDOS-Np_2	705	755	[31]	P3	500	623	[33]
PProDOT-Np_2	630	337	[31]	PCPDT-Ph	507	567.7	This work
P(F-Th)	629	306.8	[32]	PCPDT-PhOMe	532	543.9	This work

3.4 Electrochromic Device

In order to make the polymer material close to the actual application scenario and provide a key basis for commercial selection, an electrochromic device was assembled using a PCPDT-PhOMe film[Fig.8(A)]. The

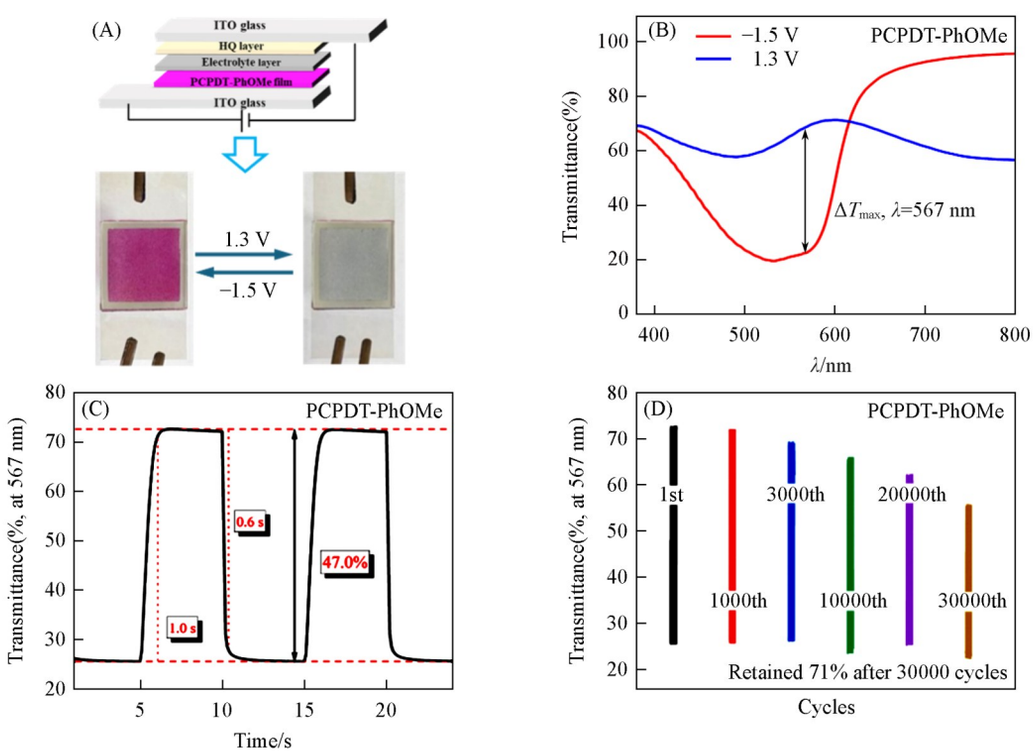


Fig. 8 Device structure diagram and color change picture(A), transmittance variation at different potentials(B), optical contrast and response time at maximum contrast wavelength(C), and cyclic stability of the device(D)

hydroquinone is colorless and transparent in the neutral state, and slightly yellow in the oxidation state, which makes it have little effect on the color change of the electrochromic layer. The assembled device with this material can well reflect the color switching of the electrochromic material itself, and its redox potential also matches the electrochromic potential of the electrochromic material. It is a suitable ion storage layer material. As shown in Fig.8(B) and (C), the device has the highest contrast at 567 nm, and achieves a fast switching speed of no more than 1.0 s at this wavelength in a suitable voltage range (coloring process is −1.5 V, bleaching process is 1.3 V), it can achieve reversible switching from magenta to transparent. In addition, the contrast of the device remains about 71% after 30000 cycles, indicating that the prototype device has favorable electrochromic performance[Fig.8(D)].

4 Conclusions

In general, two solution-processable polymers (PCPDT-Ph and PCPDT-PhOMe) based on cyclopentadithiophene (CPDT) and different benzene/dimethoxybenzene groups were synthesized. This work elaborated on a simple molecular engineering approach to modulate the optical absorption properties and adjust the color of novel electrochromic polymer materials through the substituent engineering. Compared with PCPDT-Ph, the introduction of alkoxy side chain in PCPDT-PhOMe produce a lower oxidation potential and redshifted absorption spectra owing to the stronger electron-donating and conjugated effect of dimethoxybenzene group. Benefiting from the strong electron-donating characteristics and rigid molecular configuration of the CPDT structure, both polymers exhibited low initial oxidation potential, fast response speed and relatively high coloring efficiency. Among them, PCPDT-PhOMe showed better cycle stability, and the device constructed from this polymer had favorable electrochromic properties, including fast switching time, suitable optical contrast and satisfactory cyclic stability. Consequently, this research provides a useful reference for the rational design of soluble thiophene electrochromic polymers, and confirms the application potential of PCPDT-PhOMe materials in the fields of smart windows and electronic displays.

The supporting information of this paper see http://www.cjcu.jlu.edu.cn/CN/10.7503/cjcu20250323.

References

[1] Wu W. T., Poh W. C., Lv J., Chen S. H., Gao D., Yu F., Wang H., Fang H. J., Wang H., Lee P. S., *Adv. Energy Mater.*, **2023**, *13*(18), 2204103
[2] Zhang W., Li H. Z., Elezzabi A. Y., *Adv. Funct. Mater.*, **2021**, *32*(7), 2108341
[3] Liu C. L., Yang J. K., Liu Y. L., Li S. Y., Liu H. R., *Chem. J. Chinese Universities*, **2023**, *44*(10), 20230203(柳春蕾, 杨继凯, 刘昱麟, 李思远, 刘昊睿. 高等学校化学学报, **2023**, *44*(10), 20230203)
[4] Liu R., Li Y., Hu B., Long Y., *Adv. Funct. Mater.*, **2024**, *35*(1), 2409914
[5] Hao H. Y., Wang X., Shao Z. Q., Yang R. J., *Chem. J. Chinese Universities*, **2015**, *36*(9), 1838—1845(郝红英, 王茜, 邵自强, 杨荣杰. 高等学校化学学报, **2015**, *36*(9), 1838—1845)
[6] Seo D. G., Moon H. C., *Adv. Funct. Mater.*, **2018**, *28*(14), 1706948
[7] Li W. S., Guo Y. T., Shi J. J., Yu H. J., Meng H., *Macromolecules*, **2016**, *49*(19), 7211—7219
[8] Wang J. H., Zhang L., Ma Y. X., Xie W. N., Dong J. H., Dong Y. J., Li W. J., Zhang C., *Chem. Eng. J.*, **2024**, *498*, 155278
[9] Yin Y. Y., Li W. S., Zeng X. Z., Xu P. P., Murtaza I., Guo Y. T., Liu Y. M., Li T. T., Cao J. P., He Y. W., Meng H., *Macromolecules*, **2018**, *51*(19), 7853—7862
[10] Lv X. J., Zhu X. C., Zhang L., Ouyang M., Xia M. A., Liu C. Y., Zhang C., *J. Mater. Chem. C*, **2023**, *11*(16), 5490—5497
[11] Teran N. B., Reynolds J. R., *Chem. Mater.*, **2017**, *29*(3), 1290—1301
[12] Dyer A. L., Thompson E. J., Reynolds J. R., *ACS Appl. Mater. Inter.*, **2011**, *3*(6), 1787—1795
[13] Christiansen D. T., Ohtani S., Chujo Y., Tomlinson A. L., Reynolds J. R., *Chem. Mater.*, **2019**, *31*(17), 6841—6849
[14] Christiansen D. T., Reynolds J. R., *Macromolecules*, **2018**, *51*(22), 9250—9258
[15] Collier G. S., Pelse I., Österholm A. M., Reynolds J. R., *Chem. Mater.*, **2018**, *30*(15), 5161—5168
[16] Lo C. K., Shen D. E., Reynolds J. R., *Macromolecules*, **2019**, *52*(17), 6773—6779

[17] Kim D., Yoon M., Lee J., *Polymers*, **2022**, *14*(1), 2
[18] Zhang X. F., Liu H., Chen Y., Cheng J. Z., Wang L. H., Ye D. N., Chen L., Liu S. Y., *Mater. Today. Commun.*, **2020**, *22*, 100850
[19] Wu C. G., Lu M. I., Chang S. J., Wei C. S., *Adv. Funct. Mater.*, **2007**, *17*(7), 1063—1070
[20] Raju T. B., Gopikrishna P., Iyer P. K., *RSC Adv.*, **2014**, *4*(71), 37738—37745
[21] Yang G. J., Fan J. P., Zhang K., Gu C., Li J., Kang K., Xiang C. Y., Qian L., Zhang T., *Adv. Funct. Mater.*, **2023**, *34*(17), 2314983
[22] Pi Q. Z., Bi D. Q., Qiu D. F., Wang H. W., Cheng X. F., Feng Y. Q., Zhao Q., Zhou M. D., *J. Mater. Chem. C*, **2021**, *9*(28), 8994—9000
[23] Le T. H., Kim Y., Yoon H., *Polymers*, **2017**, *9*(4), 150
[24] Li X. F., Wang X. K., You L. Y., Zhao K. J., Mei J. G., *ACS Mater. Lett.*, **2022**, *4*(2), 336—342
[25] Bulloch R. H., Kerszulis J. A., Dyer A. L., Reynolds J. R., *ACS Appl. Mater. Inter.*, **2014**, *6*(9), 6623—6630
[26] Wang J. H., Zhang L., Ma Y. X., Zhou C. J., Li J., Li W. J., Zhang C., *Electrochim. Acta*, **2024**, *477*, 143783
[27] Xu Z., Yue H. G., Wang B. Z., Zhao J. S., Wang M., Zhang Y., Xie Y., *Mater. Design*, **2020**, *194*, 108903
[28] Xing X., Wang C. F., Liu X. J., Qin L. Q., Wang E. G., Zhang F. L., *Electrochim. Acta*, **2017**, *253*, 530—535
[29] Chen X., Qu Q., *Sol. Energ. Mat. Sol. C*, **2018**, *179*, 270—275
[30] Gaupp C. L., Welsh D. M., Rauh R. D., Reynolds J. R., *Chem. Mater.*, **2002**, *14*(9), 3964—3970
[31] Karabay B., Pekel L. C., Cihaner A., *Macromolecules*, **2015**, *48*(5), 1352—1357
[32] Tong T., Mo D. Z., Deng K. R., *Electrochim. Acta*, **2023**, *470*, 143359
[33] Ming S. L., Zhen S. J., Zhang H., Zhang Z. J., Lu B. Y., Zhao J. S., Nie G. M., Xu J. K., *Polymer*, **2023**, *267*, 125675

(Ed.: L, V, K)