

LOW-POTENTIAL ELECTROSYNTHESIS OF CONDUCTING AND ELECTROACTIVE OLIGOCATECHOLBORANE WITH BLUE LIGHT-EMITTING PROPERTIES*

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Abstract Novel conducting oligocatecholborane (OCOB) with electrical conductivity of $3.73 \times 10^{-2} \text{ S cm}^{-1}$ was successfully synthesized by low-potential electropolymerization of catecholborane (COB) in boron trifluoride diethyl etherate at 0.70 V versus Ag/AgCl. FT-IR and ¹H-NMR spectra, together with the computational results, proved that COB was polymerized through the coupling at C₍₄₎ and C₍₅₎ positions and the reactive B—H bond was stable during the electrochemical polymerization. The resulting product was mainly composed of oligomers with short chain lengths by GPC and mass spectral results. The as-formed OCOB film showed good electrochemistry in monomer-free electrolytes with the electrochromic property from opaque blue to sap green. Fluorescence studies indicated that soluble OCOB can emit bright blue light under excitation of 365 nm UV light with the maximum emission at 396 nm and a fluorescence quantum yield of 0.21. The deposited OCOB also exhibited favorable thermal stability and smooth and compact morphology even at high magnifications.

Keywords: Conducting polymers; Electrochemical polymerization; Catecholborane; Boron trifluoride diethyl etherate; Fluorescence

Electronic Supplementary Material Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/s10118-013-1205-z>.

INTRODUCTION

The past decade has witnessed explosive interest and numerous unexpected discoveries in the area of conducting polymers in both fundamental understanding and applications^[1]. However, even to date, despite the large amount of work devoted to the research of conducting polymers, it is widely perceived that the design and synthesis of novel conducting polymers with unique properties sufficient for applications, such as good fluorescence properties and stable electroactivity, *etc.*, are still very necessary and significant. Nevertheless, with the vast repertoire of new techniques and thoughts at our disposal, many exciting discoveries of novel structures with new and perhaps unpredictable properties are quite expected to continue in this dynamic field.

Polyphenylene is one of the most fundamental π -conjugated architectures. In sharp contrast to the extensively studied *p*- and *m*-connected analogues^[2, 3], however, polymeric *o*-phenylenes have been recognized as an elusive class of π -conjugated compounds^[4]. Polymeric *o*-phenylenes adopt a tight helical conformation in

* The work was financially supported by the National Natural Science Foundation of China (Nos. 50963002 and 51073074), Jiangxi Provincial Department of Education (Nos. GJJ11590, GJJ10678 and GJJ12595), the Natural Science Foundation of Jiangxi Province (No. 2010GZH0041) and Jiangxi Science & Technology Normal University (No. KY2010ZY13).

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Received February 23, 2012; Revised May 30, 2012; Accepted June 11, 2012

doi: 10.1007/s10118-013-1205-z

which the densely packed phenylene units create a highly condensed π -cloud. Because they are difficult to synthesize, there are only a few reports on the preparation of short-chain *o*-phenylene oligomers^[5, 6]. Furthermore, their physical and chemical properties have largely remained unexplored. In our previous work, a series of polyalkylenedioxybenzenes were synthesized directly by the electrochemical polymerization of alkylendioxybenzenes and they showed very interesting optoelectronic properties^[7–10]. Inspired by our studies, other groups chemically synthesized *o*-phenylene polymers/oligomers and found them exhibit a surprisingly long effective conjugation length^[11]. Further work by Fukushima *et al.*^[12] and Yashima^[13] demonstrated that polymeric *o*-phenylenes undergo a redox-responsive dynamic motion and represents a long-lasting chiroptical memory. Research on *o*-phenylene polymers/oligomers is now receiving more and more attention.

Electrochemical polymerization, as one of fast and reliable conventional synthetic methods, has been widely employed for the generation of conducting polymers onto a conducting surface^[14]. Conducting polymer films prepared by this technique are usually formed in an oxidized (doped) state and can be used without further treatment. Generally, the choice of solvents and electrolytes exerts considerable effects on the structures of the electrogenerated conducting polymers and affects the orientation of the polymer chains, thus influencing the electrical, optical, mechanical and electrochemical properties of the films. In recent years, boron trifluoride diethyl etherate (BFEE), which serves not only as the solvent but also as the supporting electrolyte, is electrochemically stable over a wide potential range and has been proved to be an excellent medium for the electrochemical polymerization of aromatic compounds^[15–18]. Until to date, many conducting polymers, such as polythiophene^[15], poly(*p*-phenylene)^[16], polyfuran^[19], polyselenophene^[20], polyindoles^[21], polypyrenes^[22, 23], polybenzanthrone^[24], poly(aromatic ethers)^[25] and also ploy(*o*-phenylenes)^[9, 10], *etc.*, have been successfully electrosynthesized in BFEE and BFEE-based electrolytes.

Based on our previous work, the electropolymerization performance of a novel alkylendioxybenzene catecholborane (COB), which is an important intermediate and often used as catalyst and co-catalyst in organic synthesis, is investigated in detail herein. COB was selected as the monomer due to the following reasons: First, in the field of sensor materials, the incorporation of Lewis acidic organoboron moieties into conjugated polymers has been shown to lead to sensor signal amplification effects^[26–28]. Secondly, physical and chemical properties of organoborons are modified as the vacant *p*-orbital of the boron atom is disturbed. Generally, organoboron compounds bearing π -conjugated groups have a unique LUMO on a boron atom in which the π -conjugation is divergently extended through the vacant *p*-orbital of the boron atom. On the other hand, polymeric organoboranes were generally synthesized through chemical method and few of them through electrochemistry.

In this paper, the low-potential electropolymerization of COB led to facile electrodeposition of oligocatecholborane films. The structural characterization, electrochemistry, fluorescence and other properties of the resulting oligomer, such as morphology and thermal stability, were minutely investigated.

EXPERIMENTAL

Materials

Catecholborane (COB, 97%; Acros Organics) was used as received. BFEE (1.12–1.14 g mL⁻¹, BF₃ = 48.24%; Beijing Changyang Chemical Plant, China) was distilled before use. Tetrabutylammonium tetrafluoroborate (Bu₄NBF₄, 95%; Acros Organics) was dried under vacuum at 60°C for 24 h before use. Commercial HPLC grade acetonitrile (Tianjin Kermel Chemical Reagents Research Institute) was used directly without further purification. Perdeuterated dimethyl sulfoxide (d₆-DMSO) was purchased from Cambridge Isotope Laboratories, Inc. Other reagents were all analytical grade and used as received without further treatment.

Electrosynthesis and Electrochemical Tests

Electrochemical synthesis and examinations of OCOB were performed in a one-compartment cell with the use of a Model 263A potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. For electrochemical tests, the working and counter electrodes were Pt wire with a diameter of 0.5 mm and stainless steel wire with a diameter of 1 mm, respectively. They were placed 5 mm apart during the tests. To obtain a

sufficient amount of the polymer films for characterization, stainless steel sheets with a surface area of 10 and 12 cm² each were employed as the working and counter electrodes, respectively. These aforementioned electrodes were polished carefully with abrasive paper (1500 mesh), cleaned by water and acetone successively, and then dried in air before each experiment. An Ag/AgCl electrode directly immersed in the solution served as the reference electrode, and it revealed sufficient stability during the experiments. The typical electrolytic solution was BFEE containing 0.05 mol L⁻¹ COB. All the solutions were deaerated by a dry nitrogen stream and maintained under a slight overpressure through all the experiments. The polymer films were grown potentiostatically, and their thickness was controlled by the total charge passed through the cell, which was read directly from the current-time (*I-t*) curves by computer. After polymerization, the polymer films were washed repeatedly with anhydrous diethyl ether in order to remove the electrolyte, monomer and oligomers. For spectral analyses, the polymer was dedoped electrochemically at -0.2 V to exclude the dopants until the current passed through the cell became equally to zero (electrochemical dedoping), and then washed with anhydrous diethyl ether. Finally, the polymer films were dried at 60°C under vacuum for 6 h. The polymer was deposited on the indium-tin-oxide (ITO) coated glass for ultraviolet-visible (UV-Vis) spectral measurements.

Characterization

Infrared spectra were determined with a Bruker Vertex 70 Fourier-transform infrared (FT-IR) spectrometer with samples in KBr pellets. ¹H-NMR spectra were recorded on a Bruker AV 400 NMR spectrometer with d₆-DMSO as the solvent and tetramethylsilane as an internal standard (TMS, singlet, chemical shift: $\delta = 0.0$). Gel permeation chromatography (GPC) measurements of the soluble sample were performed in tetrahydrofuran with a Waters Breeze GPC system. Mass spectra were carried out on a HPLC-MS ZQ4000/2695 spectrometer. The electrical conductivity of the as-formed OCOB films was determined by applying a conventional four-probe technique with the pressed pellet of the sample by the use of 220 programmable current source and Keithley 2700 multimeter under computer control (Labview 7.0). UV-Vis spectra were taken by using a Perkin-Elmer Lambda 900 ultraviolet-visible near-infrared spectrophotometer. Thermogravimetric analysis (TGA) was performed with a Pyris Diamond TG/DTA thermal analyzer (Perkin Elmer) under a nitrogen stream from 290 K to 1070 K at a heating rate of 10 K min⁻¹. Scanning electron microscopy (SEM) measurements were made with a VEGA\LSU scanning electron microscope (Tescan). With an F-4500 fluorescence spectrophotometer (Hitachi), the fluorescence spectra were determined. The fluorescence quantum yield (ϕ_{overall}) in solution was measured using anthracene in ACN (standard, $\phi_{\text{ref}} = 0.27$) as a reference and calculated according to the well-known method given as Eq. (1)^[29]:

$$\phi = \frac{n^2 A_{\text{ref}} I}{n_{\text{ref}}^2 A I_{\text{ref}}} \phi_{\text{ref}} \quad (1)$$

Here, *n*, *A*, and *I* denote the refractive index of solvent, the absorbance at the excitation wavelength, and the intensity of the emission spectrum, respectively. The subscript “ref” denotes the reference, and no subscript denotes the sample. The absorbance of the samples and the standard should be similar.

RESULTS AND DISCUSSION

Electrochemical Polymerization of COB

The electrochemical performance of COB was first examined by linear sweeping voltammetry in both CH₃CN-Bu₄NBF₄ (0.1 mol L⁻¹) and BFEE, and the resulting anodic polarization curves are shown in Fig. 1. Note here that BFEE was acting as both the solvent and the electrolyte (without the addition of any other salts). It can be seen that the onset oxidation potential of COB in BFEE was approximately at 0.51 V, about 0.4 V lower than that in CH₃CN-Bu₄NBF₄ (0.1 mol L⁻¹) (0.91 V). The reason for the large descent in the onset oxidation potentials lies in the fact that BFEE can interact with the aromatic ring of these compounds, which reduced the resonance stability of the corresponding monomers through the formation of π -complexes between the monomers and BFEE, thus making electron loss from the monomers much easier^[30]. It is well known that high

oxidation potential generally makes the electropolymerization of aromatic monomers quite difficult, and also leads to some side reactions. Furthermore, the conducting polymer/oligomer films produced on the electrode are easily overoxidized during further electropolymerization. Obviously, it is beneficial to the preparation of conducting polymer/oligomer films if the polymerization potential can be decreased. From this point of view, BFEE was the better choice for the electropolymerization of COB. On the other hand, the film deposited in $\text{CH}_3\text{CN-Bu}_4\text{NBF}_4$ (0.1 mol L^{-1}) was observed to dissolve quickly during the experiments and it was very difficult to obtain sufficient amount films for characterization. Therefore, BFEE was chosen as the solvent and supporting electrolyte.

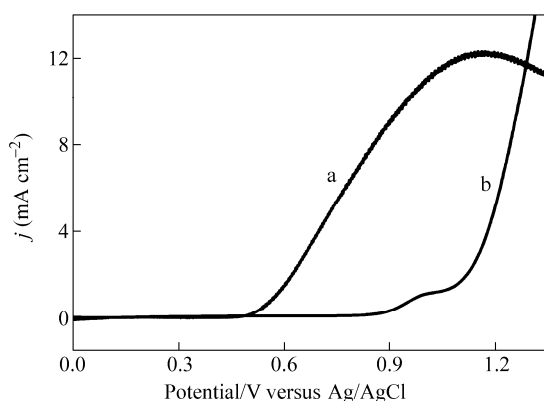


Fig. 1 Anodic polarization curves of 0.05 mol L^{-1} COB in BFEE (a) and $\text{CH}_3\text{CN-Bu}_4\text{NBF}_4$ (0.1 mol L^{-1}) (b) (Potential scan rate: 50 mV s^{-1})

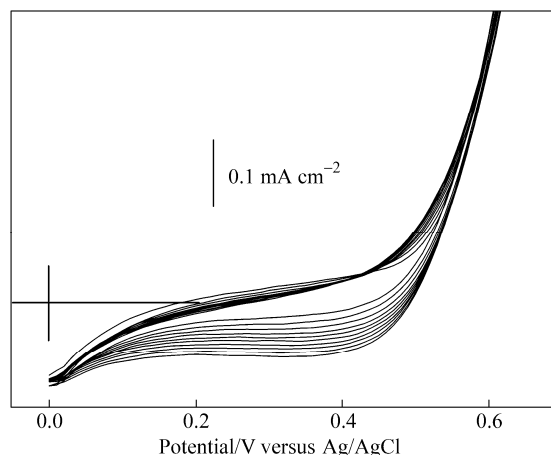


Fig. 2 Successive cyclic voltammograms of 0.05 mol L^{-1} COB in BFEE (Potential range and scan rate: $0-1.1 \text{ V}$ and 50 mV s^{-1})

Figure 2 shows the typical successive cyclic voltammograms of COB in BFEE. The CVs showed characteristic features of other conducting polymers/oligomers during potentiodynamic synthesis such as pyrene^[31] and 1-nitropyrene^[23]. In the first cycle, the anodic current began to increase at about 0.51 V , and there was a current loop between 0.51 V and 1.10 V . The formation of this loop is characteristic for nucleation processes, as reported in the literature^[32]. Also, the formation of a compact and homogeneous OCOB film blue in color on the electrode surface was observed at potentials greater than 0.51 V . As the potential scanning continued, there was an obvious reduction peak near 0.30 V . The increase of the redox wave currents implied that the amount of the oligomer on the electrode was increasing gradually. However, visual inspection during CV experiments revealed that the increasing interval between the peak current densities was very small in comparison with other aromatic compounds, indicating that it is hard for COB to deposit on the electrode by the potentiodynamic method and also this method is not suitable for large scale deposition.

Therefore, the potentiostatic electrolysis was employed to prepare OCOB films in BFEE for characterization. Considering the overall factors affecting the quality of the formed film, such as moderate polymerization rate, negligible overoxidation, regular morphology, and good adherence against the working electrode, chronoamperometry at a constant applied potential of 0.70 V versus Ag/AgCl was selected. Therefore, the OCOB films used for the characterization mentioned below were all prepared under this condition.

Electrochemistry of OCOB

In order to get a deeper insight into its electroactivity and stability, the electrochemical behavior of the OCOB-modified Pt electrode was studied by cyclic voltammetry in monomer-free BFEE and concentrated sulfuric acid, as shown in Fig. 3. It can be clearly seen that the steady-state CVs of OCOB represented broad anodic and cathodic peaks in both electrolytes. The peak current densities were proportional to the potential scanning rates (insets of Fig. 2), indicating that the redox process is nondiffusional and the electroactive material is well

adhered to the working electrode surface. Furthermore, the polymer could be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition, indicating good redox stability of the materials. The peak potential shift of CVs for conducting polymers/oligomers is hardly explained by conventional kinetic limitations such as ion diffusion or interfacial charge transfer processes. The main reasons accounting for this phenomenon are usually as follows, slow heterogeneous electron transfer, local rearrangement effect of polymer chains, slow mutual transformation of various electronic species and the electronic charging of interfacial exchange corresponding to the metal/polymer and polymer/solution interfaces, *etc*^[33]. In monomer-free BFEE (Fig. 3a), the oxidation and reduction of the as-formed OCOB film occurred in the potential range from 1.34 V and 0.35 V at the potential scan rate of 20 mV s⁻¹, whereas in concentrated sulfuric acid it could be oxidized and reduced from 0.52 V to 0.19 V (Fig. 3b). This can be mainly ascribed to the slower transfer rate of large doping anions and solvent molecules in BFEE, such as [EtO]₃BF₃⁻, than for SO₄²⁻, especially at high scan rates^[33].

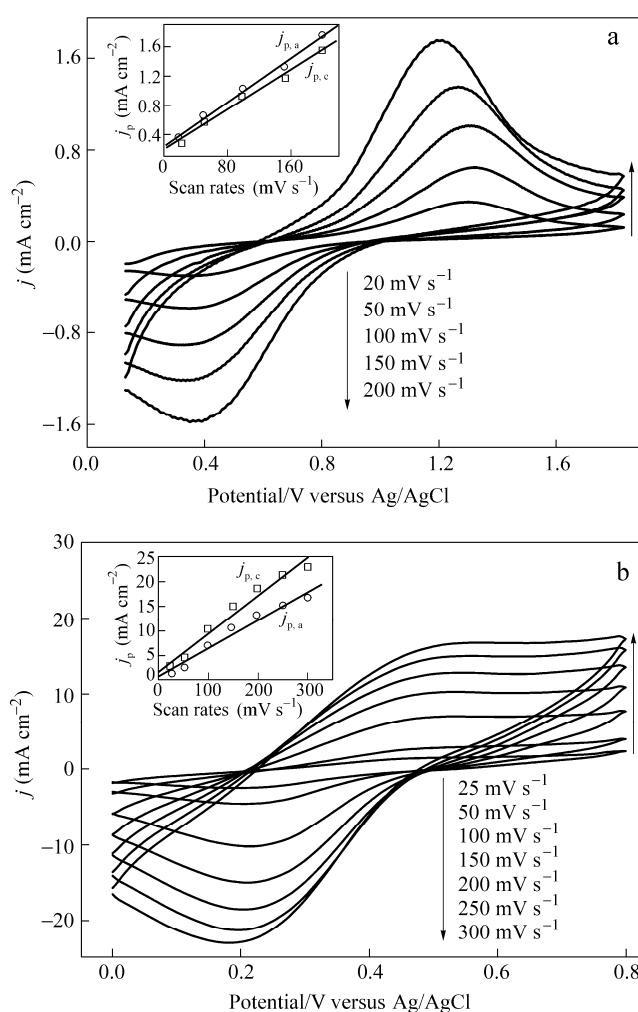


Fig. 3 Cyclic voltammograms of OCOB films in BFEE (a) and concentrated sulfuric acid (b) at different potential scan rates indicated. The OCOB film was synthesized electrochemically in BFEE at a constant applied potential of 0.70 V versus Ag/AgCl.

Structural Characterization

Infrared spectra can provide much structural information for newly-obtained polymers. A comparison of the evolution of the vibrational modes appearing in polymers and in some simple related molecules acting as references usually facilitates the interpretation of the experimental absorption spectra. In order to elucidate the structure of OCOB and interpret the polymerization mechanism, FT-IR spectra of COB and the doped OCOB were recorded, as shown in Fig. 4. From the figure, it can be clearly seen that typical peaks located at 2263, 2360 and 2510 cm^{-1} (the stretching vibration of B—H) still existed in the spectrum of OCOB, indicating the active —BH— group was stable and not destroyed during the electrochemical polymerization. Also, the stretching vibration of B—O in COB appeared at 1366 cm^{-1} , while after polymerization the same peak shifted to a higher wave number at 1378 cm^{-1} in the spectrum of OCOB. On the other hand, the peaks of OCOB at 857 and 793 cm^{-1} compared with those of COB could be assigned to the 1,2,4,5-tetrasubstituted benzene ring, implying the occurrence of the polymerization and the reaction sites may be $\text{C}_{(4)}$ and $\text{C}_{(5)}$ positions (if the polymerization occurs at $\text{C}_{(3)}$ and $\text{C}_{(6)}$ positions, the peaks of OCOB would emerge at about 760 and 720 cm^{-1} in the fingerprint region due to 1,2,3,4-tetrasubstituted benzene ring). Moreover, the peaks in the spectrum of OCOB were obviously broadened in comparison with those of the monomer, similar to those of other conducting polymers reported previously. This instance was mainly due to the resulting product composed of COB oligomers with different chain length. Their C—C skeleton vibrational peaks with different polymerization degrees have different IR shifts. These peaks overlapped one another and produced broad bands with hyperstructures. Furthermore, chemical defects on the oligomer chains resulting from the overoxidation also contributed to the band broadening of IR spectra.

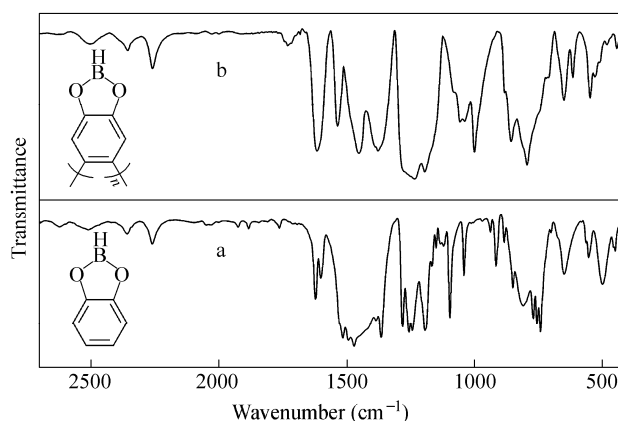


Fig. 4 FT-IR spectra of COB (a) and the doped OCOB (b)

To further investigate oligomer structure and the polymerization mechanism of COB, ^1H -NMR spectra of COB and the soluble part of doped OCOB were recorded in d_6 -DMSO, as shown in Fig. 5. There were three group proton peaks shown in the ^1H -NMR spectrum of COB (Fig. 5a). The proton lines at $\delta = 6.69$ – 6.74 and 6.56 – 6.63 could be ascribed to the protons at $\text{C}_{(4)}$, $\text{C}_{(5)}$ and $\text{C}_{(3)}$, $\text{C}_{(6)}$ positions of the benzene ring in COB. The protons at these positions showed multiple peaks because of the spin-spin splitting between them. After polymerization, the proton chemical shift at $\delta = 6.56$ – 6.63 disappeared and the another one moved to lower fields (Fig. 5b). Generally, with introducing longer conjugation length into the polymer backbone, the chemical shifts of hydrogen atoms on the aromatic rings usually move to lower fields^[34]. Therefore, this phenomenon can be ascribed to the introduction of higher conjugation lengths in the OCOB main chain. In the spectrum of OCOB, only one singlet at $\delta = 7.60$ was observed (Fig. 5b), implying that the polymerization sites were $\text{C}_{(4)}$ and $\text{C}_{(5)}$ positions. There may be two polymerization mechanisms for the electrochemical polymerization of COB, through $\text{C}_{(4)}$ – $\text{C}_{(5)}$ and $\text{C}_{(3)}$ – $\text{C}_{(6)}$ positions. If the polymerization happened through $\text{C}_{(3)}$ – $\text{C}_{(6)}$, the proton lines of the resulting product would be a doublet due to the spin-spin splitting between the protons at $\text{C}_{(4)}$ and $\text{C}_{(5)}$ positions.

Therefore, this singlet proton line at $\delta = 7.60$ can be assigned to the protons at C₍₃₎ and C₍₆₎ positions and thus the main backbone of OCOB was similar to polyacetylene (Scheme 1).

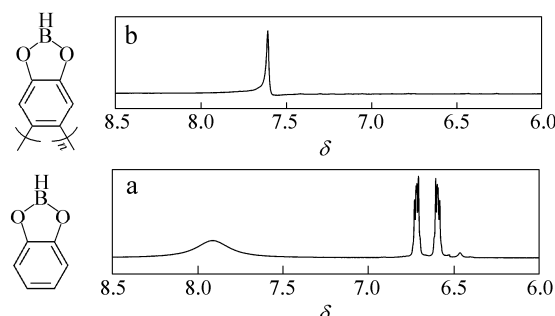
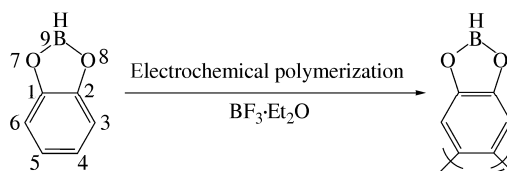


Fig. 5 ^1H -NMR spectra of COB (a) and doped OCOB (b) in d_6 -DMSO



Scheme 1 Chemical structure and electrochemical polymerization of COB

Quantum chemistry calculation has also been extensively and effectively applied to investigate the chemical structure and properties of newly obtained conducting polymers. For more information on the structure of OCOB, we optimized the geometry of COB and calculated its atomic electron density population (Table 1) and proportion of the frontier orbitals (Table 2) using the Gaussian 03 program. Note that COB was optimized without symmetry constraints using a hybrid density functional and Becke's three-parameter exchange functional combined with the LYP correlation functional (B3LYP) and with the 6-31G(d, p) basis set (B3LYP/6-31G(d, p)). Vibrational frequencies were evaluated at the same level to identify the real minimal energy

Table 1. Main atomic electron density populations for COB

Atom	Electric charge	Atom	Electric charge
C ₍₁₎	0.275867	C ₍₂₎	0.275867
C ₍₃₎	-0.111519	C ₍₄₎	-0.100154
C ₍₅₎	-0.100154	C ₍₆₎	-0.111519
O ₍₇₎	-0.448493	O ₍₈₎	-0.448493
B ₍₉₎	0.435467		

Table 2. Main composition and proportion of the frontier orbitals in COB (%)

Atom	HOMO	LUMO
C ₍₁₎	21.10424	7.903634
C ₍₂₎	21.10424	7.903634
C ₍₃₎	0.485891	29.80666
C ₍₄₎	18.81647	7.33107
C ₍₅₎	18.81647	7.33107
C ₍₆₎	-0.26734	29.80666
O ₍₇₎	7.073876	0.082321
O ₍₈₎	7.073876	0.082321
B ₍₉₎	5.792276	9.752637

HOMO and LUMO are defined as the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively.

structures. As shown in Table 1, the results of the main atomic electron density populations revealed negative electric charges at all the positions of the benzene ring, implying that these atoms may donate electrons during electrochemical polymerization through radical cation intermediates. According to the molecular orbital theory, the reaction among the active molecules mainly happens on the highest frontier molecular orbital and the near orbital. For COB, the HOMO proportions at C₍₄₎ and C₍₅₎ positions were higher than those for all other reactive atoms (Table 2). All these calculations demonstrated that the polymerization of COB would happen preferentially at C₍₄₎ and C₍₅₎ positions, in well accordance with FTIR and ¹H-NMR spectral results. The possible polymerization mechanism of COB is shown in Scheme 1.

Solubility, Molecular Weight, Electrical Conductivity and UV-Vis Spectra

The as-formed films were obtained in the doped state and dark blue in color. When they were dedoped by 25% ammonia, their color changed to dark green. It is very interesting that both doped and dedoped OCOB films are partly soluble in many common organic solvents, such as acetonitrile, DMSO, dichloromethane, tetrahydrofuran, chloroform, and even methanol, ethanol, acetone, diethyl ether, *etc.* This nice solubility of OCOB may facilitate its applications in various fields.

GPC measurements of the soluble part of the dedoped oligomer in tetrahydrofuran demonstrated that the soluble part of OCOB showed a number-average molar mass (M_n) of about 1056 and a weight-average molar mass (M_w) of 1093 in tetrahydrofuran, with a narrow molecular weight distribution of 1.04. Furthermore, the composition of dedoped OCOB films in acetonitrile was also characterized by HPLC-MS ZQ4000/2695 spectrometry, as shown in Fig. S1. The spectra were very complex but the m/z values varied in the range from about 105 to 995, indicating that the soluble part of the as-formed OCOB was mainly composed of relatively short-chain oligomers with about 1–8 repetitive units, of which trimers and tetramers contributed a large proportion. These results indicated that the soluble OCOB was composed of relatively short-chain oligomers.

The electrical conductivity of the pressed pellet of doped OCOB film by the conventional four-probe technique was measured to be about $3.73 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature, relatively lower than those of some other conducting polyalkylenedioxybenzenes, such as poly(1,2-methylenedioxybenzene) (0.8 and 0.1 S cm^{-1})^[7, 10] and poly(1,2-ethylenedioxybenzene) (0.17 S cm^{-1})^[10]. The low conductivity can be mainly attributable to the short chain length of the as-formed OCOB mentioned previously.

UV-Vis spectra of COB and the soluble part of dedoped OCOB in acetonitrile are shown in Fig. 6. The monomer showed a characteristic absorption peak at 296 nm (Fig. 6, spectrum a), whereas both of the doped and dedoped OCOB (Fig. 6, spectra b and c) exhibited a strong absorption band in the same region with the maximum shifted to 304 nm. At the same time, the doped OCOB film displayed another broad absorption from 590 nm to 820 nm with a peak at 697 nm. This could be attributable to the existence of conductive species, such as polarons or bipolarons. Moreover, it can be clearly seen that due to the increase in the conjugated chain length, the overall absorption of the oligomer tailed off to more than 380 nm in comparison with that of the monomer (308 nm for COB). These spectral results confirmed the occurrence of electrochemical polymerization among the monomers and the formation of a conjugated polymer. On the other hand, OCOB also exhibited good electrochromic properties between the doped and dedoped state, from sap green to opaque blue (inset of Fig. 6).

Fluorescence Properties

Our previous results showed that polyalkylenedioxybenzenes displayed good blue light-emitting properties with relatively high quantum yields^[7, 10]. Therefore, the emission spectra of the monomer and the dedoped oligomer were determined in acetonitrile, as shown in Fig. 7. It is observed that the emission peak for COB emerged at 319 nm (Fig. 7, spectrum a), similar to those of 1,2-methylenedioxybenzene (320 nm) and 1,2-ethylenedioxybenzene (310 nm), whereas a maximum emission at 396 nm characterized the spectrum of dedoped OCOB (Fig. 7, spectrum b). In comparison with the monomer, the emission peak of the oligomer revealed a 77 nm bathochromic shift because of the elongation of the oligomer's delocalized π -electron chain sequence. Besides, the wider emission range of the oligomer is reasonable, because the oligomer OCOB is composed of oligomers with different chain lengths, and the emissions of these components with different

polymerization degrees show different spectral ranges. These spectra overlap one another and produce wide emission spectra of OCOB. Moreover, the emission peak of OCOB also showed a slight red shift compared with that of poly(1,2-methylenedioxybenzene) (385 nm)^[10] and poly(1,2-ethylenedioxybenzene) (383 nm)^[10] in the same electrolyte.

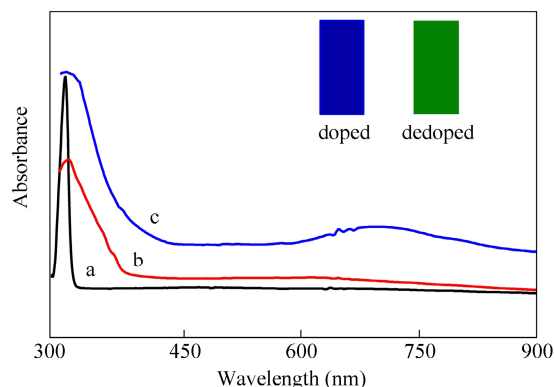


Fig. 6 UV-Vis spectra of COB (a), dedoped OCOB (b) in ACN, and doped OCOB (c) deposited electrochemically on the ITO glass from BFEE at the constant applied potential of 0.70 V versus Ag/AgCl

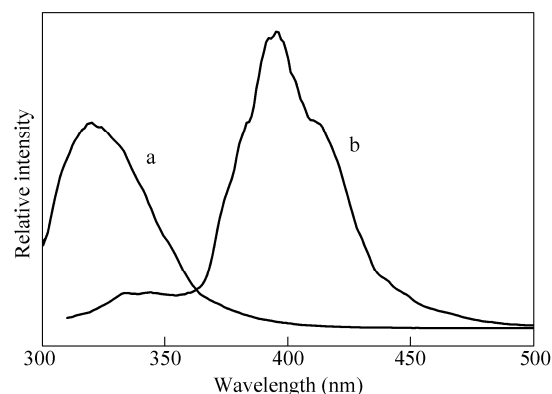


Fig. 7 Emission spectra of COB (a) and dedoped OCOB film (b) in ACN

Meanwhile, it is also very interesting to find that soluble OCOB dissolved in common organic solvents, such as methanol, ethanol, acetone, acetonitrile, diethyl ether, DMSO, *etc.*, can all emit strong blue-green photoluminescence when exposed to 365 nm UV light, as shown in Fig. 8, whereas the monomer COB showed no emission. According to Eq. (1), the fluorescence quantum yield (ϕ_{overall}) of COB was calculated to be only 0.03, whereas that of the soluble dedoped OCOB was improved to be 0.21, 6 times more than that of the monomer. This value of OCOB is similar to the analogues reported previously, such as poly(1,2-methylenedioxybenzene) (0.13)^[7, 10], poly(1,2-ethylenedioxybenzene) (0.27)^[10], *etc.* Taking all these aspects together, OCOB is typically a blue-light-emitting oligomer, and may find applications in various fields as a promising candidate in organic light-emitting diodes.

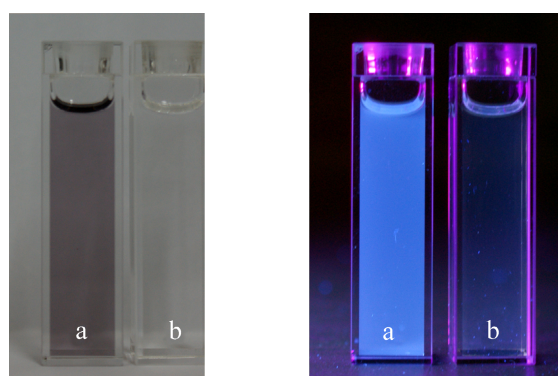


Fig. 8 Photoluminescence of COB (b) and the soluble part of the dedoped OCOB (a) under visible light (left) and 365 nm UV irradiation (right) (Solvent: acetonitrile)

Thermal Analysis

Thermal degradation behaviors of conducting polymers are very important for their potential applications. To investigate the thermal stability of the newly obtained oligomers, thermogravimetric analytical experiments were

performed under a nitrogen stream, as shown in Fig. 9. It can be seen that at low temperatures ($T < 480$ K), the oligomer initially underwent a weight loss of about 8.2%. Such a weight loss was closely related to water evaporation and other moisture trapped in the oligomer. The following prominent degradation between 480 and 625 K (37.1%) was probably caused by the degradation of $-\text{BH}-$ and $-\text{OBHO}-$ groups on the oligomer. Simultaneously, from the differential thermogravimetry (DTG) curve, the corresponding maximal decomposition existed at 578 K. With the gradual increasing of the temperature, there was another prominent decomposition between 625 K and 1060 K of about 17.3%. This weight loss was closely related to the decomposition of the skeletal chain structure and the overflow of some structural fragments decomposed from OCOB. In addition, when the temperature reached 1060 K, the residual weight was even about 37.4%. These results indicate favorable thermal stability of OCOB due to the high thermal stability of benzene rings in the main chain.

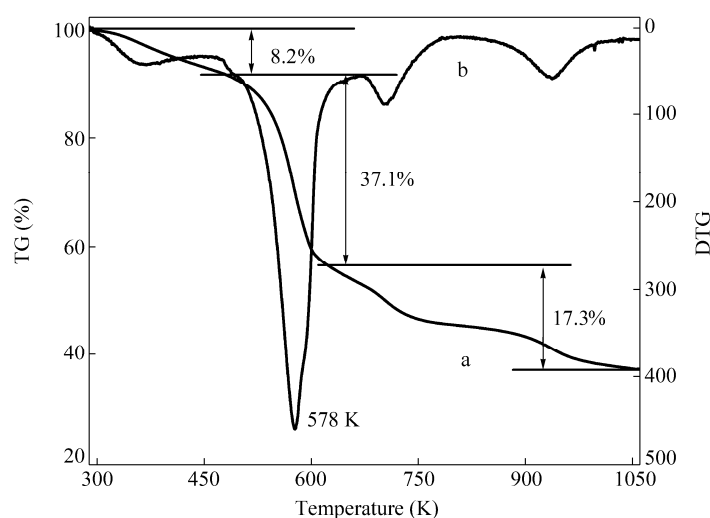


Fig. 9 TG (a) and DTG (b) curves of dedoped OCOB

Morphology

Surface morphologies of conducting polymers are closely related to their properties, such as electrical conductivity, redox activity and stability, *etc.* Therefore, the surfaces of both the doped and dedoped OCOB films deposited on the ITO electrodes were observed by scanning electron microscope (SEM), as shown in Fig. 10. Macroscopically, in both the doped and the dedoped states, OCOB films appeared to be smooth and

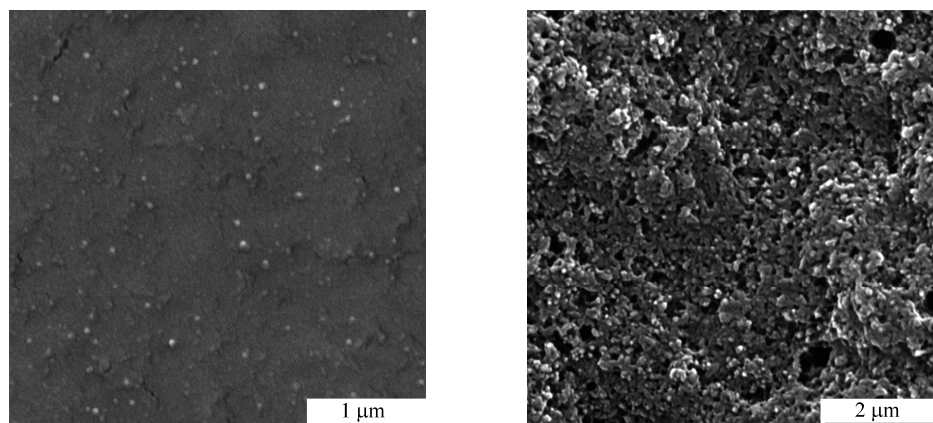


Fig. 10 SEM images of doped (left) and dedoped (right) OCOB deposited electrochemically on the ITO glass from BFEE at the constant applied potential of 0.70 V versus Ag/AgCl

homogeneous. Microscopically, even at high magnifications, the surface of the doped oligomer film was still rather smooth, continuous and compact. This morphology of compact OCOB film was extremely beneficial to improve its electrical conductivity and electron transfer capability, thus making it a good candidate for various applications, such as ion-selective electrodes and matrix for hosting catalyst particles, *etc*^[35–37]. On the contrary, after dedoping at a constant applied potential of -0.2 V, the surface of OCOB film became uneven and porous, quite different from that of the doped polymer. This phenomenon is mainly due to the migration of counter anions out of the oligomer film and also the gradual solubility of OCOB from the electrode to the solution during the dedoping processes, which destroy the smooth surface of doped OCOB films. However, the porous morphology of the dedoped OCOB facilitates the movement of doping anions into and out of the polymer film during the doping and dedoping process, in well accordance with the good redox activity of the oligomer films in the monomer-free electrolytes.

CONCLUSIONS

For the first time, a new *o*-phenylene π -conjugated oligomer with good redox activity and stability was synthesized electrochemically by low-potential electropolymerization of COB. Full characterization of the resulting oligomer showed that OCOB exhibited favorable solubility, electrical conductivity, good thermal stability and uniform morphology. Additionally, fluorescent studies demonstrated that soluble OCOB is a blue light-emitter with its maximum emission at 396 nm and a high fluorescence quantum yield of 0.21. Also, it can emit bright blue light under excitation of 365 nm UV light. All these results indicate that OCOB is very promising as sensory and optoelectronic material and may find application in electrochemical sensors and organic electronic devices. More importantly, structural characterization proved that the polymerization occurred at C₍₄₎ and C₍₅₎ positions of the benzene ring to form an *o*-phenylene oligomer, thus making the main backbone of OCOB similar to polyacetylene. On the other hand, the reactive $-BH-$ group on the main chain of OCOB could be easily post-modified by further reaction, which should enable the tuning of film characteristics for specific enhancement of thin-film properties, including film composition, conductivity, homogeneity, redox potentials and luminescence properties.

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