Journal Pre-proof

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PII: S0167-7322(19)33552-4

DOI: https://doi.org/10.1016/j.molliq.2019.111896

Reference: MOLLIQ 111896

To appear in: Journal of Molecular Liquids

Received Date: 25 June 2019

Revised Date: 14 September 2019

Accepted Date: 9 October 2019

Please cite this article as: Y. Guo, D. He, A. Xie, W. Qu, Y. Tang, J. Shang, R. Zhu, Preparation and characterization of a novel poly-geminal dicationic ionic liquid (PGDIL), *Journal of Molecular Liquids* (2019), doi: https://doi.org/10.1016/j.molliq.2019.111896.

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Preparation and characterization of a novel poly-geminal dicationic ionic liquid (PGDIL)

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6 Abstract: 1,4-bis(3-(m-aminobenzyl)imidazol-1-yl)butane bis(hexafluorinephosphate), a novel geminal 7 dicationic ionic liquid (GDIL) containing anilino groups has been synthesized to prepare a novel poly-geminal 8 dicationic ionic liquid film by electro-polymerization. The morphology and structure of the PGDIL film were 9 analyzed by SEM and FTIR, and a possible polymerization mechanism of GDIL on an Au electrode surface was 10 determined to be 3D instantaneous nucleation. The existence of polyaniline-like units in the PGDIL chain was 11 confirmed by FTIR, indicating that the anilino groups of GDIL were electro-polymerized on the surface of the Au 12 electrode using the chronoamperometry method. The electrochemical performance of the PGDIL film in phenol 13 was studied by cyclic voltammetry, and it was determined that the PGDIL film electrode promoted enhanced 14 phenol electrocatalysis compared to the untreated Au electrode. This work extends the application range of poly ionic liquids and associates ionic liquids with conductive polymers. Where further studies on other physical and 15 16 chemical properties of polymers will be necessary.

17 Keywords: Geminal dicationic ionic liquid; Poly-ionic liquid; Electro-polymerization; Polyaniline

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1 1. Introduction

2 Poly ionic liquids (PILs), unlike conventional polymers, is a polymer that contains at least one ion center in a 3 polymer chain and a repeating unit similar to a common ionic liquid structure. They are a kind of functional 4 polymer materials which combine the properties of polymers and ionic liquids [1] and can be used as catalysts for 5 catalytic reactions by introducing the groups with catalytic activity into their molecular structures. Salamone and 6 coworkers first reported the polymerization of several vinylimidazolium-based PILs in 1973 [2]. In general, there 7 are two main routes to prepare PILs. The first one is the direct radical polymerization of IL monomers, which is 8 the most convenient and commonly employed approach. Green et al. [3] prepared a series of alkyl-substituted 9 vinylimidazolium PILs using a free-radical polymerization method and further investigated the impact of the alkyl 10 chain length on the thermal stability and ionic conductivity of PILs. Based on this method, Sun et al. [4] prepared 11 a porous quaternary phosphonium-based PIL that showed a hierarchical structure and excellent amphiphilicity. 12 The second route is the post-polymerization modification of polymer with IL monomers. Post-polymerization is 13 usually finished in the presence of reactive chemical groups, such as amino groups and sulfhydryl groups. Han et 14 al. [5] reported a PIL-modified hybrid monolithic column, which was designed and synthesized using 15 polymerizable ionic liquids with catalytic active groups as the monomer. PILs with multiple monomer link 16 polymer structure are prepared by the polymerization of polymerizable groups or unsaturated groups such as C=C 17 in the monomer [6, 7]. However, most of the studies involving ionic liquids deal with the unique physicochemical 18 and solvation properties of monocationic ionic liquids (MILs). Multifunctional ionic liquids such as dicationic 19 ionic liquids (DILs) and tricationic ionic liquids, which can extend the horizon of applications of ionic liquids, 20 have not yet been studied to a high degree.

21 DILs, a new type of ILs are considered as combination of three structural moieties: (1) cationic head groups; 22 (2) a linkage chain; and (3) the counter anions [8]. Compared to the traditional monocationic ionic liquids [9-14], 23 DILs can be classified as homoanionic dicationic ionic liquids and heteroanionic dicationic ionic liquids. These 24 DILs can further be categorized as symmetrical and asymmetrical DILs for both homoanionic and heteroanionic 25 DILs. Homoanionic dicationic ionic liquids are typical DILs, which consist of a dication and two identical anions. 26 Symmetrical or geminal dicationic ILs (GDILs) can be synthesized joining two same cation, such as imidazolium 27 or pyrrolidinium, which may contain cyclic or aliphatic chain via either a rigid or a flexible spacer. A common 28 spacer is an alkyl chain [15, 16]. Armstrong and co-workers [14] studied structure and properties relationship by 29 synthesizing 39 imidazolium-based and pyrrolidinium-based dicationic ILs. The head groups were linked with an 30 alkyl chain (from 3 to 12 carbons long), and hence, reacted with four different traditional anions. The thermal stability of these ILs in the range of -4 to >400° C, which were found to be greater than those of most traditional monocationic ILs. GDILs have the more unique physical and chemical properties and solvation characteristics and can be used as separation material [17], surfactants [18] and catalyst candidates [19,20], while still have not yet been studied heavily to the best of our knowledge [21, 22]. The same is true of poly-GDILs (PGDILs).

5 The application of PILs modified electrodes in electrocatalysis of organic pollutants has attracted extensive 6 PIL interest and attention recently [23]. Jian Hu [24] reported а cross-linker-based 7 (poly(1,4-butanediyl-3,3'-bis-l-vinylimidazolium dibromide)) for the sensitive detection of 4-nonylphenol. It not 8 only has the designability of ionic liquids (ILs) but also realizes the solidification of ILs, improves the utilization 9 ratio of ILs, and solves the difficulty of inconvenient storage of ILs as liquid. At the same time, its specific surface 10 area and reaction sites are enlarged because of the structure of polymer, which enhance the electrocatalytic effect 11 of phenols on the electrode [25, 26].

12 The most common approach toward the formation of PILs is direct free radical polymerization of the 13 unsaturated C=C in IL monomers. Polyaniline (PANI) is one of the most attractive materials among a variety of 14 conducting polymers due to its unique electrical properties, environmental stability, and easy fabrication process, 15 which is the result of the polymerization of aniline monomer. This material has been widely selected as electrode 16 active materials due to its good electrical conductivity and flexible functionality [24]. In this work, with the 17 introduction of anilino groups into the GDIL structure, a novel GDIL 18 (1,4-bis(3-(m-aminobenzyl)imidazol-1-yl)butane bis(hexafluorinephosphate)) is synthesized to prepare a novel 19 PGDIL with polyaniline-like structure. It is expected that the PGDIL film have the advantages of both polyaniline 20 and ionic liquids.

21 **2. Experimental**

22 **2.1 Main reagents and instrumentation**

m-nitrobenzyl chloride; imidazole; acetonitrile; ethyl acetate; 1,4-dibromobutane; zinc powder; ammonium
hexafluorophosphate; alumina (1.0µm, 0.3 µm, 0.05 µm); metallographic sandpaper; sodium dihydrogen
phosphate; acetic acid; sodium acetate trihydrate; citric acid; sodium chloride; sodium carbonate; sodium
bicarbonate; boric acid; sodium tetraborate; potassium chloride; potassium ferrocyanide; potassium ferricyanide;
phenol. The experimental reagents are analytical pure and the water used in the experiment is double distilled
water.

Heat-collecting type constant temperature magnetic heating stirrer (CJJ 78-1); Rotary evaporator (R.1002);
 Field emission scanning electron microscope (JSM-6700F); Ultrasonic cleaner (SK 5200HP); Infrared
 Spectrophotometer (TJ270-30A); NMR spectrometer (INOVA-400); Automatic double distilled water distillation

apparatus (Shanghai Asia-Pacific Glass instrument Company); Electrochemical workstation (IVIUMSTAT,
 IVIUM Technologies BV); Electrochemical research experiment using classical three-electrode system: working
 electrode is Au electrode; The reference electrode is Ag/AgCl electrode (self-made and the auxiliary electrode is
 platinum wire electrode).

5 2.2 Synthesis of 1,4-bis(3-(m-aminobenzyl)imidazol-1-yl)butane bis(hexafluorinephosphate)

6 ([C₄(m-ABIM)₂][PF₆]₂)

All experiments were performed under a nitrogen atmosphere, and the experimental reagents were analytical pure, and the water used in the experiment was double distilled water. The synthesis of $[C_4(m-ABIM)_2][PF_6]_2$ (GDIL) is shown in Scheme 1.

Imidazole (0.2 mol, 13.616 g) and KOH (13.44 g) were dissolved in 50 mL acetonitrile in a three-mouth flask, and a mixture of m-nitrobenzyl (0.2 mol, 34.316 g) and acetonitrile (50 mL) was added in drops. The reaction mixture was refluxed and stirred for 24 h at 55 °C. After that, 100 mL of water was added and separated the liquid into a brown oily substance. 1-(3-nitrobenzyl) imidazole was obtained by ethyl acetate extraction and rotary evaporation with a yield was of 67 %.

15 0.2 mol 1-(3-nitrobenzyl) imidazole was dissolved in 100 mL acetonitrile, and 0.1mol 1,4-dibromobutane 16 was added dropwise. The reflux reaction was carried out at 65 °C with stirring for 24 h. After the reaction, the 17 solvent was dried and the solid was washed with ethyl acetate several times. It was dried to produce a yellowish 18 solid powder, 1,4-bis(3-(3-nitrobenzyl)imidazol-1-yl)butane bromide ($[C_4(m-NBIM)_2][Br]_2$) at a yield of 57 %.

19 0.1 mol [C₄(m-NBIM)₂][Br]₂ and 0.4 mol Zn powder were added to a three-mouth flask with 80 v% 20 acetonitrile aqueous solution as the solvent. 0.1 mL 33% FeCl₃ aqueous solution was added as the catalyst and 21 then refluxed with stirring at 70 °C for 4 h. After the reaction was completed, the reaction liquid was filtered. After 22 separating solvent and removing impurities from the filtrate and drying under vacuum at 40 °C, 23 1,4-bis(3-(3-aminobenzyl)imidazol-1-yl)butane bromide was obtained as a yellowish solid powder (yield 30%).

An aqueous solution of ammonium hexafluorinephosphate was gradually added to the aqueous solution of $[C_4(m-ABIM)_2][Br]_2$ (the molar ratio of NH₄PF₆ and $[C_4(m-ABIM)_2][Br]_2$ was 2:1). After stirring for 5 h at 60 °C, the mixture was filtered to obtain a solid and via washing and vacuum drying $[C_4(m-ABIM)_2][PF_6]_2$ was obtained as a yellowish solid (yield 72%). ¹H NMR (DMSO, 400 MHz, ppm): δ 9.45(s, 4H); 8.39(s, 2H); 8.28(d, 4H); 7.55-8.15(m, 8H); 5.55(s, 4H); 4.23(t, 4H); 2.08(m, 4H).



Scheme 1 The synthesis of [C₄(m-ABIM)₂][PF₆]₂ (GDIL)
Density functional theory (DFT) simulation was performed using the Gaussian 09 software package. The
calculation was carried out using the DFT method with Becke's three-parameter hybrid exchange functionals and
the Lee-Yang-Parr correlation functional (B3LYP) employing the 6-31G (d, p) basis set for all atoms [27, 28]. The
possible 3D molecular structure model is shown in the Fig. 1. The structure of [C₄(m-ABIM)₂]²⁺ consists of
zigzag bands of molecule[29].



8 9

Fig. 1 The optimized structures of the $[C_4(m-ABIM)_2]^{2+}$ at the B3LYP/6-31G (d, p) level.

10 2.23 Preparation of poly-[C₄(m-ABIM)₂][PF₆]₂ (PGDIL)

11 An electrochemical tri-electrode system was introduced for electrochemical polymerization, in which Au, 12 Platinum wire, and Ag/AgCl electrode were used as the working electrode, counter electrode, and reference 13 electrode, respectively. The treated Au working electrode was placed in acetonitrile solution containing 0.01 mol/L $[C_4(m-ABIM)_2][PF_6]_2$ and 0.1 mol/L sodium perchlorate (supporting electrolyte), and the poly- $[C_4(m-ABIM)_2][PF_6]_2$ (PGDIL) film was prepared on the surface of Au electrode by means of chronoamperometric polymerization at constant potential of 1.2 V for 1800 s. The prepared PGDIL film was rinsed repeatedly with double distilled water, then dried under 50 °C in the vacuum drying chamber. All electrochemical experiments were performed at ambient room temperature under a nitrogen atmosphere, and the water used in the experiment was double distilled water.



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Fig. 2 Current vs. time transient during the potentiostatic electropolymerization of GDIL at potential of 1.2 V. Inset: comparison of the experiment curve with theoretical curves from the Scharifker–Hills model

10 Chronoamperometry is an important diagnostic technique for the initial stage of electrocrystallization [30]. 11 Fig. 2 shows a current transient (CTT) recorded during the polymerization of GDIL monomer at 1.2V. The 12 electropolymerization process should be hardly affected by other reactions. The CTT can be divided into three 13 regions. In the first region (t < 2 s), the decrease in oxidation current is related to charging of the double layer due 14 to the specific adsorption of GDIL on the Au electrode. The second region corresponds to the increase in the 15 oxidation current up to a maximum, which is typical of nucleation and growth processes. The third region 16 corresponds to the decrease in the oxidation current, which is typical of a diffusion controlled process. An analysis 17 of the CTT was performed by fitting the experimental data to a dimensionless theoretical curve for crystal 18 nucleation and diffusion controlled growth in three dimensions (3D), as proposed by Scharifker and Hills [31]. 19 The instantaneous and progressive theoretical transients are given by Eqs. (1) and Eqs. (2), respectively:

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$$\frac{i^2}{i_m^2} = \frac{1.9542}{t/t_m} \{1 - \exp[-1.2564(t/t_m)]\}^2$$
(1)

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$$\frac{i^2}{i_m^2} = \frac{1.2254}{t/t_m} \{1 - \exp[-2.3367 (t/t_m)^2]\}^2$$
(2)

In the equation, i_m and t_m represent the maximum current density and its corresponding time, respectively. The experiment data are fitted as shown in the inset of Fig. 2 Inset. The experimental curve conforms to the theoretical curve of the instantaneous nucleation model. Therefore, it can be concluded that instantaneous nucleation predominated at the oxidant peak potential for the electropolymerization of GDIL.

5 2.4 Electrochemical properties of PGDIL film

6 The electrochemical properties of PGDIL film modified electrode were investigated by electrochemical 7 impedance spectroscopy [32]. The prepared PGDIL/Au electrode was placed in 5.0×10^{-3} mol/L Fe(CN)₆^{3./4-} 8 solution with 0.1 mol/L KCl as the electrolyte for cyclic voltammetry(CV) test and AC impedance test 9 respectively, Platinum wire was used as the counter electrode, and an Ag/AgCl electrode (self-made) was used as 10 the reference electrode. The CV scanning rate was 0.05 V/s and the scanning range was -0.2~0.6 V. The 11 electrochemical impedance frequency ranges from 100000 to 0.01 Hz, and the sine wave signal amplitude is 5 12 mV.

The Au electrode and PGDIL/Au film modified electrode were used as working electrodes, and stirred and enriched for 3 min at open circuit potential, respectively, and cyclic voltammetry tests were carried out at a scanning rate of 0.5 V/s in the range of 0~1 V potential. The electrochemical behaviors of the Au electrode and PGDIL/Au electrode in NaH₂PO₄-C₆H₈O₇ (pH=5) buffer solution containing 0.15 mmol/L phenol were studied. After each test, the phenol adsorbed on the surface of the electrode can be removed for continuous test by cyclic voltammetry scanning in a blank base solution at a scanning rate of 0.1 V/s for 10 cycles. All electrolytes were deoxygenated w ith nitrogen before testing in order to avoid the interference of oxygen in the solution to the test.

20 **3. Results and discussions**

Fig. 3(A) is a photo map of the PGDIL powder scanning electron microscope. As shown in the picture, the PGDIL powder is composed of homogeneous, stacked, spherical particles, which is similar in shape to most conductive polymers. The PGDIL membrane is loose and porous, which is beneficial to the adsorption of contaminants in the film.

In order to gain further insight into the structure of the PGDIL and GDIL, the IR spectrum of the polymer powder was collected, as shown in Fig. 3(B). In the FTIR spectra of PGDIL, the bands at 3158 cm⁻¹ and 3106 cm⁻¹, which are attributed to the C–H ring stretching vibration of the aromatic rings (imidazolium and benzene) [33], are clearly visible, and then shift to low-frequency regions, vibrating 3057 and 2999 cm⁻¹, respectively. Since more hydrogen bonds(C–H…F) were formed after polymerization, the C–H bond length increased, the bond force constant decreased, and the absorption wavenumber shifted red [34]. 3556 cm⁻¹ and 3452 cm⁻¹ signified the stretching vibration band of N–H (primary amines), the shoulder band at 3324 cm⁻¹ as the N–H frequency doubling peak of the bending vibration, while 3462 cm⁻¹ was the stretching vibration band of N–H (secondary amines), and the shoulder band 3324 cm⁻¹ depicted the N–H frequency doubling peak of bending vibration [35].



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Fig. 3 (A) SEM diagram of PGDIL. (B) The IR spectra of GDIL and PGDIL. (C) Schematic diagram of PGDIL molecular structure (Hydrogen atoms not shown for clarity)

7 Comparing the red curve (GDIL) with the black curve (PGDIL), the peak at 1312 cm⁻¹ may be attributed to the C-N stretching vibration band of ph-NH₂, and the peaks in the range of 1700 cm⁻¹ to 1400 cm⁻¹ belong to the 8 9 N-H deformation vibration (1609 cm⁻¹) and the stretching vibration band of C=C and C-C in aromatic rings, 10 imidazole ring deformation at 924 cm⁻¹, P-F stretching vibration and N-H (primary amines) out-of-plane bending 11 vibration at 830 cm⁻¹ (broad peak) [36], C-(CH₂)₂-C skeletal vibration at 739 cm⁻¹, C-H (1,3-di substituted 12 benzene ring) out-of-plane bending vibration at 682 cm⁻¹ are observed respectively in the infrared spectra of the GDIL monomer [37]. While in the infrared spectra of PGDIL, the peak at 1329 cm⁻¹ belongs to the C–N stretching 13 14 vibration of the benzene-quinone ring variant, the peak at 1250 cm⁻¹ is assigned to the conjugate C=N stretching vibration in the quinone ring structure, and 1108 cm⁻¹ belongs to the N=O=N, O=N⁺H=B and B-N⁺H-B 15

stretching vibration [38], an imidazole ring deformation at 920 cm⁻¹, P–F stretching vibration at 835 cm⁻¹ (sharp peak), which means the $-NH_2$ groups participate in the polymerization reaction and convert into $-NH_-$ or $-N_=$, the C–(CH₂)₂–C skeletal vibration at 744 cm⁻¹, C–H (1,3,5-tri substituted benzene ring) out-of-plane bending vibration at 652 cm⁻¹ are observed, respectively [37]. However, the infrared spectra of PGDIL is quite different to that of GDIL in the range of 1700 cm⁻¹ to 1400 cm⁻¹ due to the benzenoid diimine and quinoid diamin structures formed by polymerization of anilino groups of GDIL which is similar to that of polyaniline (as shown in Fig. 3(C)) [39].

8 Combined with the infrared spectra above, it can be determined that the polymer formed by the successful 9 polymerization of aniline groups of GDIL monomer has a benzenoid diimine and quinoid diamin structure, similar 10 to that of polyaniline, and it is a partially oxidized and reduced structure. In addition, the synthesis process of 11 PGDIL is shown in Scheme 2.





12 13

Scheme 2 The synthesis process of PGDIL.

Fig. 4(A) is a cyclic voltammetry curve of bare Au and PGDIL/Au electrode in 5.0×10^{-3} mol/L Fe(CN)₆^{3./4-} solution. The ability of the film to block electrons can be determined by the reversibility of redox peaks and the peak current, which is to detect the change in properties before and after electrode modification. As the diagram shows, Fe (CN)₆^{3./4-} probes on the Au and PGDIL/Au electrode surface all have obvious redox peaks, but there are great differences in the peak types. There is a pair of obviously reversible redox peaks on the bare Au electrode, while on the PGDIL/Au modified electrode, the reduction peak current and the anodic peak current are obviously reduced, the peak-peak potential difference increases, and the degree of irreversibility decreases, which indicates that the polymer film modified on the electrode provides the Fe $(CN)_6^{3/4-}$ probe molecule to encounter greater obstacle, but the apparent presence of redox peaks also indicates that the modified polymer film is relatively loose and has better conductive properties.



Fig. 4 (A) The cyclic voltammetry curves of PGDIL/Au and Au in the presence of 5.0 mmol L^{-1} Fe(CN)₆^{3-/4-} with 0.1 mol L^{-1} KCl as electrolyte. (B) The EIS plots of PGDIL/Au and Au in the presence of 5.0 mmol L^{-1} Fe(CN)₆^{3-/4-} with 0.1 mol L^{-1} KCl as electrolyte. Inset is the Randle's equivalent circuit

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8 Fig. 4(B) shows the AC impedance spectra of the Au and PGDIL/Au at potential of 0.3 V. It can be seen 9 from the graph that both the bare gold electrode and the polymer modified electrode have a semicircle at high 10 frequency and a straight line at low frequency region, which illustrates that the reaction processes of the Au and 11 PGDIL/Au electrode are controlled by electrochemical reaction and diffusion. The real parts of the impedance 12 diagrams are the same, indicating that the solution ohm resistances are the same during all electrode reactions, 13 namely the electrolytes. The semicircle diameter of the high frequency region of the modified electrode is larger 14 than that of the bare gold electrode, which indicates that the charge transfer resistance of the electrolyte ions in the 15 film modified gold electrode is greater than that of the bare gold electrode. The circular diameter of the modified 16 electrode in high frequency region is larger than that of the bare gold electrode, which indicates that the charge 17 transfer resistance of the electrolyte ions in the film modified gold electrode is greater than that of the bare gold 18 electrode. This is because the modified film is less conductive than the gold electrode and obstructs the electrons 19 in reaching the electrode through the membrane layer. In the process of dynamic control at the low frequency 20 region, the relative velocity of reaction in kinetic process of the modified electrode is higher than that of the bare 21 gold electrode because the frequency of each modified electrode is greater than that of the bare gold electrode. 22 The slope of the straight line in the low frequency region of the bare gold electrode is larger than that of each 23 modified electrode, indicating that the diffusion resistance of the modified gold electrode is larger than that of the 24 bare Au electrode. The illustration is an equivalent circuit model based on the electrochemical impedance data fitting of the modified electrode, where R_s represents the solution resistance, and R_{ct} represents the charge-transfer resistance, which to some extent, reflects the polymer film on the surface of the electrode. With a larger R_{ct} value, the electronic transmission must overcome a larger barrier (denser and thicker film layer), which, in turn, leads to a more difficult reaction. C_{dl} represents a double-layer capacitance and W represents the Warbury impedance.

5 Fig. 5(A) shows the cyclic voltammetry curves of the PGDIL/Au and Au electrodes in buffer solution. It can 6 be seen from the diagram that the two electrodes have no peak current response on the cyclic voltammetry 7 measured in the phenol-free buffer, and the curve current is close to $0 \mu A$, which indicates that the buffer solution 8 can be used as the supporting electrolyte for the electrocatalytic reaction. When the concentration of phenol in the 9 buffer is 0.015 mol/L, there is almost no oxidation peak on the bare gold electrode, and the electrochemical 10 response is very weak, while there is a oxidation peak at 0.7 V on the PGDIL/Au electrode, its oxidation peak 11 type is obvious, and the electrochemical reaction of phenol on the electrode is completely irreversible. The PGDIL 12 membrane has stronger adsorption capacity and higher enrichment efficiency to allow the phenol concentration on 13 the electrode surface to increase, and thus the oxidation peak current will increase.



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Fig. 5 (A) Cyclic voltammograms of PGDIL/Au and bare Au electrode with and without 0.015 mol/L phenol (Scan rate is 0.5 V/s). (B) CVs of 15mmol/L phenol with various scan rates (0.1~0.9 V·s⁻¹). Inset: corresponding relationships between the anodic peak currents and scan rates
 To further study the mass transfer characteristics of phenol on the PGDIL/Au composite membrane modified

electrode, the cyclic voltammetry curves of the composite membrane modified electrode in 0.015mol/L phenol solution were measured when the scan rate was in the range of 0.1~0.9 V/s, as shown in Fig. 5(B). It can be seen from the diagram that with the increase of the scan rate, the oxidation peak current increases and the oxidation peak potential shifts positively, which indicates that the oxidation of phenol on the PGDIL/Au electrode is 1 kinetically-controlled. Furthermore, using the oxidation peak current (i_p) as the vertical coordinate and the scan 2 rate (v) as the transverse coordinate, the $i_p \sim v$ curve was obtained (Fig. 5(B) Inset). It was shown that I_p and v are in 3 good linear relationship, which shows the reaction is controlled by the adsorption process. The linear equation is 4 I_p =1.352+8.497*v, r²=0.9981.

According to the laviron equation [40] for the irreversible reaction process controlled by adsorption, $E_p = E^0 - \frac{RT}{\beta nF} \ln \frac{RTK^0}{\beta nF} + \frac{RT}{\beta nF} \ln v$, $\beta = 1 - \alpha$, the number of electrons involved in the reaction can be obtained from the slope of the relation between E_p and $\ln v$, that is, $\frac{RT}{(1-\alpha)nF} = 0.0437$, where α is the transfer coefficient. For the irreversible adsorption control process of 0.5, it is known that T = 298.15 K, R = 8.314, F = 96500 C/mol, and the number of electrons involved in the reaction is n = 1.175, close to 1. In other words, when the scanning rate is 0.5 V/s, the electrocatalytic oxidation of phenol on PGDIL film modified electrode is controlled by single electron transfer.

12 Based on the above results, as shown in Fig. 6, it was speculated that the electrocatalytic mechanism of 13 phenol is that phenol is adsorbed on PGDIL film modified electrode first, and with the rise of electrode potential, 14 phenol adsorbed on the PGDIL film modified electrode is electrochemically activated and loses electrons to form 15 active intermediates with positive centers. This process is the control step, and then the proton is quickly lost to 16 form a large number of phenoxy radicals. It is an initial oxidation step, the continued electrochemical oxidation of 17 the phenoxy radicals would first result in the formation of hydroquinone (or catechol) and then to benzoquinone. 18 The further reactions of the quinones are slow reactions with the main products being organic acids (maleic, 19 formic, oxalic acid), and finally mineralized to carbon dioxide and water [41, 42].



Fig. 6 Electrocatalytic mechanism of phenol

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1 4. Conclusion

2 A novel ionic liquid 1,4-bis(3-(m-aminobenzyl)imidazol-1-yl)butane bis(hexafluorinephosphate), containing 3 anilino groups, was synthesized and characterized. The FTIR and NMR results showed that the synthesized 4 product was consistent with the target ionic liquid. Furthermore, using the above ionic liquid as a monomer, a 5 novel PGDIL film was successfully prepared via a chronoamperometry method. The SEM result revealed that the 6 morphology of the PGDIL was loose and porous composed of homogeneous, spherical, and stacked particles, 7 which was beneficial to the adsorption of contaminants on the film. The existence of polyaniline-like units in the 8 PGDIL chain was confirmed by FTIR, indicating that the anilino groups of GDIL was electro-polymerized on the 9 surface of the Au electrode by the chronoamperometry method. The electrochemical performance of PGDIL film 10 was studied, and it is found that the PGDIL flim modified electrode showed improved effects on phenol 11 electrocatalysis compared than that of the Au electrode. It can be expected to be used in electrochemical catalytic 12 reaction of other organic compounds. It extends the range of poly ionic liquids and associates ionic liquids with 13 conductive polymers again, but the related chemical and electrochemical properties need to be studied further.

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Journal

Highlights

- Anilino groups was introduced into ionic liquid structure to prepare poly-ionic liquid
- The ploy-ionic liquid containing polyaniline-like units
- The modified electrode suggested to give a high sensitivity in detection phenol

Conflict of interest statement

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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