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# A Diazonium Salt-Based Ionic Liquid for Solvent-Free Modification of Carbon

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A novel ionic liquid that consists of *p*-butylbenzenediazonium ions and bis(trifluoromethanesulfonyl)amidates ($Tf_2N^-$) has been synthesized as a task-specific ionic liquid for the solvent-free modification of carbon materials. The use of anions $Tf_2N^-$ is the key to rendering the hydrophobicity, low liquidus temperature, and ionicity to this novel molten salt. This diazonium salt has a melting point of 7.2 °C and a moderate electric conductivity of 527 μs/cm at 25 °C. The thermal stability of this diazonium ionic liquid has been investigated by high-resolution thermogravimetric analysis (HRTGA). The compound is stable up to about 90 °C in nitrogen, which is only 10 °C less than its solid tetrafluoroborate counterpart. The modification of carbon materials has been carried out through both thermal and electrochemical activations of diazonium ions to generate free radical intermediates without the use of any solvent. The surface-coverage loadings of 3.38 μmol/m$^2$ and 6.07 μmol/m$^2$ for covalently attached organic functionalities have been achieved by the thermally induced functionalization and electrochemically assisted reaction, respectively.

## Introduction

There has been a recent resurgence of interest in ionic liquids (IL) for various applications in catalysis,[1,2] separation,[3–6] material synthesis,[7,8] and electrochemistry.[9–12] The use of non-volatile organic solvents and the development of solvent-free procedures in organic synthesis are two important approaches towards green chemistry.[1,2,13] Room-temperature ionic liquids (RTILs) are generally considered as alternative solvents for greener organic synthesis based on their exclusive physicochemical properties, such as negligible vapor pressures, excellent ionic conductivities, and tunable hydrophobicities.[14]

It has been well known that one of the most convenient synthesis methods for the covalent surface modification of carbon,[15–17] metal,[18] and semiconductors[19,20] is through the use of diazonium compounds.[21] Arenediazonium ions are chemically or electrochemically reduced into radicals that covalently attach to carbon, metal, and silicon surfaces, forming covalently bonded dense functional layers. The chemical stabilities of arenediazonium salts depend on counteranions.[21] For example, arenediazonium tetrafluoroborate compounds are the most stable diazonium salts but normally solid at room temperature.[21] Accordingly, the reactions of these diazonium salts are usually carried out at solutions phases in the presence of solvents. The yields of diazonium reactions vary with the chemical properties of the solvents. Solvent-free reactions of diazonium salts not only are favored on the basis of green chemistry,[22] but also can improve the synthesis yields because of increased concentrations of diazonium ions.[21] Tour and co-workers have developed a solvent-free diazonium reaction through an in-situ generation of diazonium salts by the reaction of substituted aniline with alkyl nitrite.[23] More recently, they reported the use of the conventional ionic liquids as solvents for diazonium salts for surface functionalization of carbon nanotubes.[24] Single-walled carbon nanotubes were successfully exfoliated and functionalized as individuals in aryldiazonium salts in the presence of ionic liquids and $K_2CO_3$. Herein, we describe the development of a new class of stable, conductive, and hydrophobic room-temperature ionic liquids based on diazonium salts tailored for chemical and electrochemical functionalization of carbon materials, metal surfaces, or semiconductor interfaces.

## Results and Discussion

The synthesis protocol for diazonium-based RTILs is schematically shown in Scheme 1. The essence of this methodology is to generate diazonium ions, which can be stabilized by noncoordinating, hydrophobic, and floppy bis(trifluoromethanesulfonyl)amide anions ($Tf_2N^-$).[25] The resulting diazonium ionic liquid is stable at room temperature and can be employed to modify monolithic porous carbon rods through thermal decomposition or electrochemical reduction without use of any solvent. The anions are introduced through a metathesis reaction involving lithium bis(trifluoromethanesulfonyl)amidate ($LiTf_2N$) and a diazonium salt. The noncoordinating nature of $Tf_2N^-$ is the key

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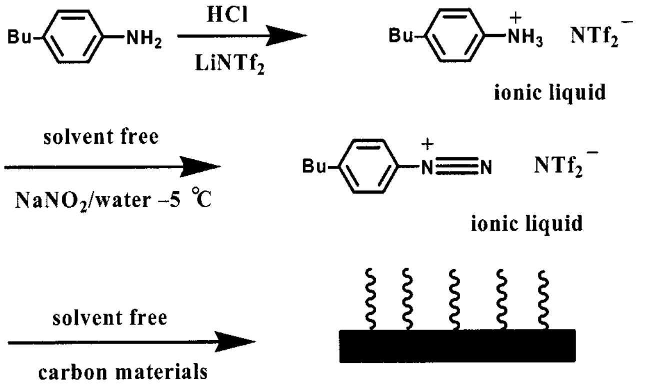
to the stability of the resulting diazonium ions, whereas its hydrophobicity contributes to the immiscibility of the resulting IL with aqueous phases.[25] The unique flexible structure of $Tf_2N^-$ renders the resulting IL with a low melting point. This synthetic approach gives significances to two aspects: 1) the design of ionic liquids for solvent-free synthesis and functionalization involving diazonium ions and 2) the development of highly conductive media for electrochemical functionalization through diazonium ions. To the best of our knowledge, this is the first report of the ionic liquids based on diazonium ions, which are a new class of task-specific ionic liquids with a tailored reactivity.[6]



Scheme 1. Schematic illustration of a synthetic approach for the diazonium ionic liquid and its application for the chemical modification of carbon materials.

The synthesis of *p*-butylbenzenediazonium bis(trifluoromethanesulfonyl)amidate was chosen to demonstrate the basic protocol. The conversion from *p*-butylanilinium bis(trifluoromethanesulfonyl)amidate to *p*-butylbenzenediazonium bis(trifluoromethanesulfonyl)amidate is basically quantitative with the overall yield of more than 97%. The spectra of FTIR, H$^1$NMR, and C$^{13}$ NMR were described in the supporting information. The melting point of *p*-butylbenzenediazonium bis(trifluoromethanesulfonyl)amidate is 7.2 °C, which is much higher than that of *p*-butylanlinium bis(trifluoromethanesulfonyl)amidate. The increase in the melting point from the ammonium salt to the diazonium salt is attributed to the packing arrangement of the corresponding ion pairs. The ion pair of diazonium salt is more compact than that of the ammonium salt. The density of *p*-butylanlinium bis(trifluoromethanesulfonyl)amidate is 1.39 g/cm$^3$, whereas the density of *p*-butylbenzenediazonium bis(trifluoromethanesulfonyl)amidate is 1.61 g/cm$^3$. This observation is consistent with the more dense structure of the latter IL.

The stability of the diazonium ions is highly dependent on conjugate anions.[21] In Figure 1 the high-resolution thermogravimetric analysis (HRTGA) curves of *p*-butylbenzenediazonium salts with counteranions of bis(trifluoromethanesulfonyl)amide (ionic liquid) and tetrafluoroborate (solid) are shown. The pyrolysis experiments were carried out under nitrogen. These HRTGA curves clearly show that the diazonium ionic liquid is stable at room temperature. The diazonium-based RTIL is stable up to 89.9 °C in $N_2$ but less stable than the corresponding solid tetrafluoroborate salt. The weight loss of the bis(trifluoromethanesulfonyl)amide salt at 90 °C is about 6%, which can be attributed to the release of $N_2$ (theoretical weight loss: 6.3%). The corresponding tetrafluoroborate salt decomposes at a temperature only 10 °C higher than the bis(trifluoromethanesulfonyl)amide salt. Induced by the release of $N_2$, the diazonium salts produce aryl cations, which can be used to covalently modify carbon materials.[21] Accordingly, the decomposition onset of the diazonium ions can be correlated to the activation temperature of the diazonium salts.

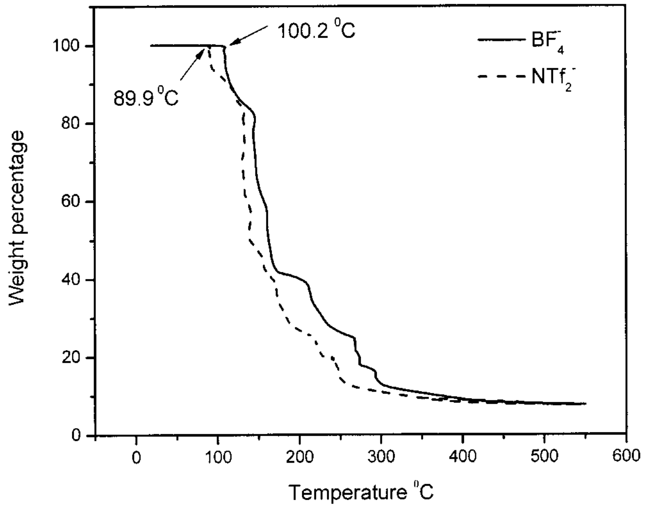


Figure 1. High-resolution thermogravimetric analysis (HRTGA) curves of two *p*-butylbenzenediazonium salts with anions of bis(trifluoromethanesulfonyl)amide (ionic liquid, represented by dash line), and tetrafluoroborate (solid, represented by solid line).

The chemical functionalization of carbon materials was conducted with a porous carbon rod soaked in *p*-butylbenzenediazonium bis(trifluoromethanesulfonyl)amidate and heated overnight at 85 °C. A covalently bonded organic layer formed on the carbon surface. The synthesis of the porous carbon rod was described in our previous work.[17,26] The use of 85 °C allows a slow, controllable, and uniform functionalization based on the HRTGA analysis. The diazonium IL decomposes slowly at this temperature. The thermally produced aryl cations were covalently attached to the carbon surface, forming a covalently bonded organic layer.[27] The surface-modified carbon was washed with copious amount of ethanol and DI water. After being dried overnight at 80 °C in a vacuum oven, the sample was grounded and loaded on a diamond attenuated total reflectance (ATR) sample holder with a compression module for FTIR measurement. In contrast to an unmodified carbon rod, the IR spectrum of the modified carbon has a set of peaks in the range of 600 to 3500 cm$^{-1}$ (Figure 2). The C–H stretching vibration of the butyl group renders a set of peaks from 2819 to 2980 cm$^{-1}$.[17] The *p*-substituted aromatic ring gives rise to three strong peaks at 824, 1516, and 1623 cm$^{-1}$.[17]

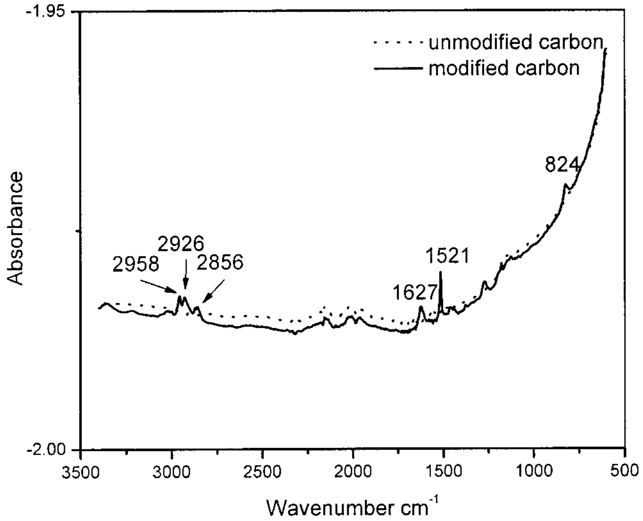


Figure 2. FTIR spectra of unmodified (dash line) and 4-butylphenyl-modified (solid line) porous carbon rods.

In addition to the thermal activation, the electrochemical functionalization with diazonium salts can be readily achieved at room temperature through electrochemical reduction.[16] The radical intermediates are generated by the dissociation reaction induced by electron transfer.[16,21] Because the traditional diazonium salts are solid, the electrochemical functionalization requires an anhydrous organic solvent, which can dissolve the diazonium salts and provide the mobility of ions. The diazonium ionic liquid has an intrinsic electric conductivity of 527 µs/cm at 25 °C, which eliminates the use of any solvent. Therefore, the electrochemical reduction of the diazonium salt can be carried out without the use of solvents. This solvent-free electrochemical approach is not limited to the modification of carbon and can be readily extended to functionalize other conductive substrates. A pair of porous carbon rods was used as working and counter electrodes, respectively. A polished Pt wire was employed as a quasi-reference electrode. The electrochemical cell was purged with an argon flow at 10 cm$^3$/min for 30 minutes. The electrochemical reduction was carried out at –0.8 V vs. Pt on the cathode under 5 cm$^3$/min argon flow. The resulting organic layer gradually reduced the conductivity of the carbon surface during functionalization, because of the self-limiting growth of a surface monolayer. The density of the monolayer was characterized by thermogravimetric analysis (TGA).[23] The weight loss at temperature 200 to 600 °C is attributed to the thermal decomposition of the surface functionalities.[23] As seen in Figure 3, the weight loss of electrochemically modified carbon is 5.85%, which is higher than 3.26% of the chemically modified carbon. Accordingly, the modification density of the electrochemical modification is much higher than that of the chemical modification. The electrochemical reduction was carried out under relatively milder conditions than that of the chemical modification. Therefore, the solvent-free electrochemical functionalization with the diazonium IL could be more uniform than the thermally activated chemical functionalization.

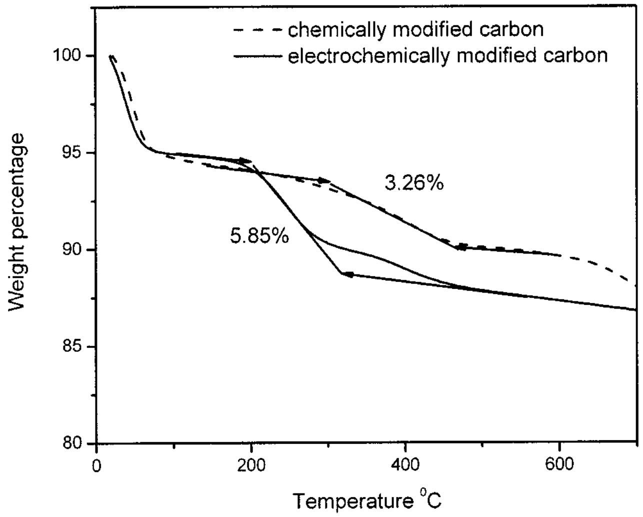


Figure 3. Thermogravimetric analysis (TGA) curves of chemically (dash line) and electrochemically (solid line) modified carbon rods.

## Conclusions

By using bis(trifluoromethanesulfonyl)amidate as conjugate anion, *p*-butylaniline forms an ammonium ionic liquid, which can be subsequently transformed into *p*-butylbenzenediazonium ionic liquid through a biphasic reaction with aqueous sodium nitrite solution. The resulting diazonium ionic liquid is stable at room temperature and preserves the reactive nature and conductivity of the diazonium ion. The liquid nature of the diazonium ionic liquid enables the solvent-free modification of carbon by either thermal decomposition or electrochemical reduction of the diazonium ion. A dense organic layer was covalently attached to the carbon surfaces of a porous carbon rod.

## Experimental Section

In a typical run, *p*-butylaniline (0.01 mol) was protonated in HCl solution (2 M, 20 mL). A solution of lithium bis(trifluoromethanesulfonyl)amidate (0.01 mol) in water (10 g) was added into the protonated *p*-butylaniline solution. A pale yellow liquid formed immediately at the bottom of the reaction vessel. The hydrophobic yellow liquid was separated and washed with a copious amount of deionized (DI) water. The product, the IL *p*-butylanilinium bis(trifluoromethanesulfonyl)amidate, was characterized by FTIR, $^1$H NMR, and $^{13}$C NMR (see the supporting information). In order to check the reaction yield, the product was dried in a vacuum oven at 60 °C. The liquid recovered was 4.84 g, giving a yield of 98%. This product can be directly used for the synthesis of the corresponding diazonium IL. *p*-Butylanilinium bis(trifluoromethanesulfonyl)amidate was cooled to –5 °C in ice-salt bath. A solution of sodium nitrite (1 g) in DI water (10 g, pre-cooled to –5 °C) was added dropwise into the *p*-butylanilinium bis(trifluoromethanesulfonyl)amidate under magnetic stirring. The oily phase became yellow and viscous. The product was kept at –5 °C for additional 30 minutes to ensure the completion of the reaction. The ice/salt bath was then removed, allowing the slow rise of temperature to room temperature. A yellowish liquid was recovered at the bottom of the beaker and washed with DI water. The product was freeze-dried overnight, which gave 4.90 g of the ionic liquid. The water content was measured by Karl Fischer titration (for details see the supporting information). The final product contains less than 0.013% water. The other impurity contents (0.0048% lithium, 0.098% sodium, and 0.063% chloride) were measured by ion chromatography. No detectable anilinium cations were found in the final diazonium-based IL.

**Supporting Information** (for details see the footnote on the first page of this article): FTIR, $^{1}$H NMR, $^{13}$C NMR, calculation of ligand density, and Karl Fischer titration.

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