



Two novel binuclear sulfonic-functionalized ionic liquids: Influence of anion and carbon-spacer on catalytic efficiency for one-pot synthesis of bis(indolyl)methanes

Nader Ghaffari Khaligh^{a,*}, Taraneh Mihankhah^b, Mohd Rafie Johan^a, Juan Joon Ching^a

^a Nanotechnology and Catalysis Research Center, 3rd Floor, Block A, Institute of Postgraduate Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia

^b Kharazmi University, Faculty of Engineering, Civil Engineering Department, Tehran, Iran

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ABSTRACT

Two new binuclear sulfonic-functionalized ionic liquids with four-carbon spacer were synthesized and their structures were characterized by FTIR, MS, ¹H and ¹³C NMR; then some physical properties and pH of the aqueous solution of new task-specific ionic liquids were determined. Their dual solvent-catalytic activity were studied for the synthesis of bis(indolyl)methanes under mild conditions. The catalytic activity of these ionic liquids were compared with some ionic liquids derived from pyrazinium, piperazinium, benzimidazolium, imidazolium mono- or di-cation containing chloride and hydrogen sulfate as counter anion under optimized conditions. It was proved that the new ionic liquids containing two sulfonic imidazole moieties with four-carbon spacer as well as hydrogen sulfate as acidic counter anion were superior to the previously reported ionic liquids.

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1. Introduction

Ionic liquids become alternative solvents, catalysts and extracting agents due to environmental perspectives including low vapor pressure, thermal and chemical stability, high ionic conductivity, tunable polarity and designable properties, immiscibility with some organic solvents simplified separation of products and potential reusability [1–5]. The majority of ionic liquids reported for organic transformations and catalysts have focused on imidazole or pyridine-based derivatives. Brønsted acidic ionic liquids (BAILs) containing SO₃H-functionalized on imidazole ring and an acidic counter anion as well as protonated imidazolium cation have been known to show dual solvent-catalyst properties with satisfactory conversion rates and selectivity for multicomponent reactions [6–9]. Nowadays, ionic liquids are used as an unconventional media for sustainable organic synthesis that allows selective separation of the desired products and catalysts in different phases, thus evading tedious and overpriced procedures which consume high volumes of toxic and volatile organic solvents. In this perspective, designing organic reactions in ionic liquid media is another attractive area in green chemistry [10,11].

The ionic liquid can be often recovered and reused. Often, the ionic liquid can be removed by water from the organic products using a simple workup. When a precious metal catalyst is used in the reaction, this procedure cannot be performed. In the other approach, the organic

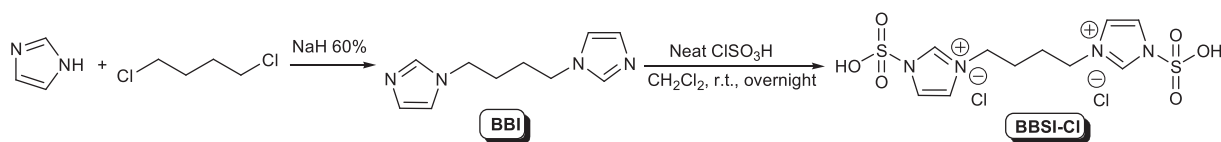
products can be extracted by nonpolar organic solvents and the remained ionic liquid can be concentrated and then directly recharged with new reactants for another run.

Bis(indolyl)methanes (BIMs) as a derivative of the substituted indoles have been achieved growing attention because of their broad spectrum of biological and pharmaceutical activities and their utility for drug design [12–14]. BIMs have been utilized as the colorimetric chemosensor for aspartate and glutamate in water as well as a simple tris-(indolyl)methane reported to detect fluoride anions by naked eye [15,16]. Therefore, a variety of synthetic protocols have been reported for the preparation of BIMs, and the electrophilic substitution reaction of indoles with carbonyl compounds in the presence Brønsted or Lewis acids is one of the most simple and important protocols. Lewis acids are often moisture sensitive as well as they will be deactivated by nitrogen atom present in indole and bis(indolyl)methane [17].

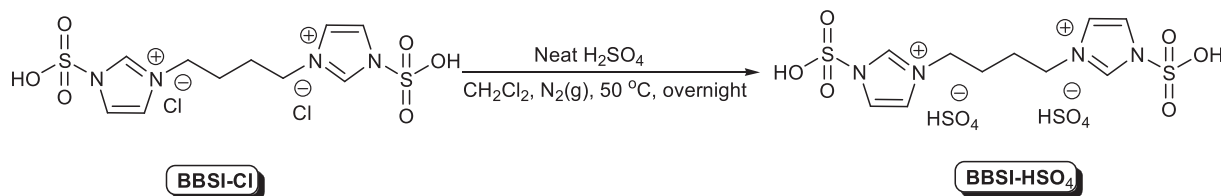
In pursuit of our studies on the preparation of new sulfonic-functionalized acidic ionic liquids and their applications as solvent or catalyst in a variety of the organic transformations [18–24], herein, two new binuclear sulfonic-functionalized ionic liquid (TSIL) with chloride and hydrogen sulfate counter anion were synthesized and their structures were characterized by FTIR, MS, ¹H and ¹³C NMR. The physical properties of new TSILs were determined and their dual solvent-catalytic activity was investigated for the synthesis of the symmetric BIMs under mild conditions. Also, the effect of the presence of the four-carbon spacer and acidic anion on the catalytic activity of these TSILs were studied in comparison with some previously reported sulfonic-functionalized ILs.

* Corresponding author.

E-mail address: ngkhaligh@gmail.com (N.G. Khaligh).



Scheme 1. Synthesis of 1,1'-butylenebis(3-sulfo-3H-imidazol-1-ium) chloride **BBSI-Cl**.



Scheme 2. Synthesis of 1,1'-butylenebis(3-sulfo-3H-imidazol-1-ium) hydrogen sulfate **BBSI-HSO₄**.

2. Results and discussion

2.1. Synthesis of 1,1'-butylenebis(3-sulfo-3H-imidazol-1-ium) chloride **BBSI-Cl** and 1,1'-butylenebis(3-sulfo-3H-imidazol-1-ium) hydrogen sulfate **BBSI-HSO₄** and the characterization of their structures

1,1'-Butylenebis(3-sulfo-3H-imidazol-1-ium) chloride (**BBSI-Cl**) was prepared in two steps (Scheme 1). At the first step, two equivalents of imidazole were alkylated by one equivalent 1,4-dichlorobutane in DMSO in the presence of two equivalent NaH as a base reagent at

room temperature. The resulting white solid 1,1'-(1,4-butanediyl)bis(imidazole) (**BBI**) then was transformed into **BBSI-Cl** using two equivalent neat chlorosulfonic acid as the sulfonylating reagent in CH_2Cl_2 at room temperature overnight. The resulting ionic liquid was isolated as viscous colorless liquid and the structure of **BBSI-Cl** was characterized by FTIR, MS, ^1H and ^{13}C NMR.

Then, neat sulfuric acid was added dropwise to **BBSI-Cl** in CH_2Cl_2 over a period of 2 min at room temperature. The resulting mixture was stirred for overnight at 50 °C under a continuous flow of nitrogen to remove the hydrogen chloride gas released during the reaction (Scheme 2). The

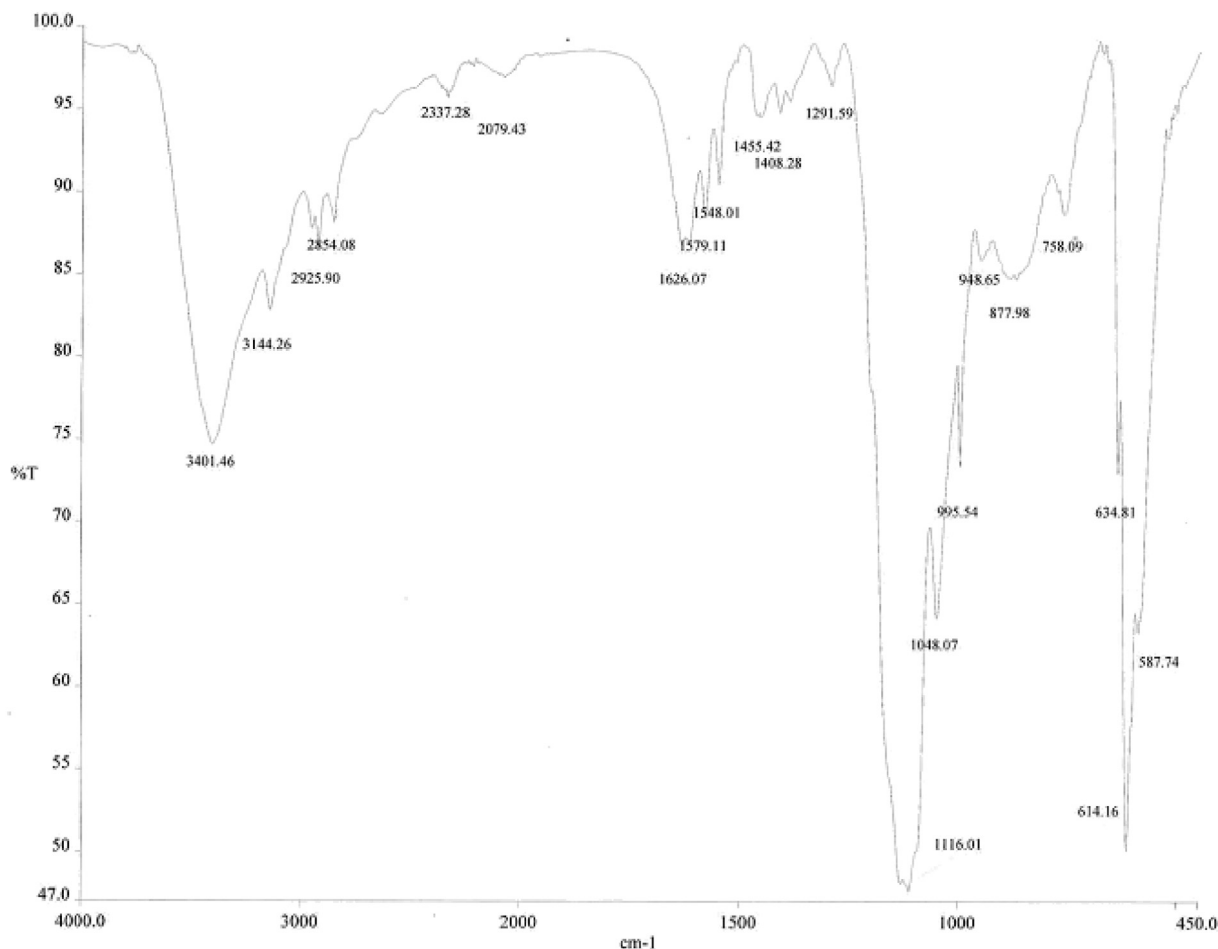


Fig. 1. FTIR Spectra of 1,1'-butylenebis(3-sulfo-3H-imidazol-1-ium) chloride **BBSI-Cl**.

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