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Novel SO_3H-Functionalized Ionic Liquids Based on Benzimidazolium Cation: Efficient and Recyclable Catalysts for One-Pot Synthesis of Biscoumarin Derivatives

**Wei Li · Yu Wang · Zhizhong Wang ·
Liyi Dai · Yuanyuan Wang**

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Abstract In this article, a new group of SO_3H-functionalized ionic liquids based on benzimidazolium cation was synthesized and used as environmentally benign catalysts for the one-pot synthesis of biscoumarin derivatives. The ionic liquids showed high catalytic activities and reusabilities with good to excellent yields of the desired products. H_0 (Hammett function) values and the minimum-energy geometries of SO_3H-functionalized ionic liquids were determined and the results revealed that the acidities and catalytic activities of ionic liquids in the synthesis of biscoumarin derivatives were related to their structures.

Keywords SO_3H-functionalized ionic liquids · Benzimidazolium cation · Biscoumarin derivatives · Minimum-energy geometries · Ab initio calculation

1 Introduction

Coumarins play an important role in both natural and synthetic organic chemistry because of their potential applications in fragrance, pharmaceutical and agrochemical industries [1]. Coumarin derivatives especially biscoumarins have been widely used as anticoagulants, antibiotics, antitumor drugs, HIV protease inhibitors as well as additives in food and cosmetics [2–4]. To date, available synthesis methods of biscoumarins include Pechmann, Perkin, Knoevenagel, Reformatsky, and Wittig reactions. Among these, the Knoevenagel reaction is the most commonly applied one, in which different types of acid catalysts such as sulfuric acid, phosphorus pentoxide, aluminum chloride, iodine, trifluoroacetic acid were employed [5–7]. Most of these previous studies, however, involved harsh reaction conditions, longer reaction times, alternative energy source like ultrasound [8], microwave [9] and corrosive reagents, which are undesirable for industrialization purposes. Therefore, it was thought worthwhile to develop an economic and mild condition method to overcome those drawbacks of traditionally employed processes. In recent years, ionic liquids (ILs) are receiving a widespread attention as environmentally acceptable reaction medium due to their advantageous properties. The potential of ILs as green "designer solvents and/or catalysts" has become a practical target for reducing waste and hazards by avoiding traditional volatile organic solvents and corrosive catalysts [10–14]. Previous studies on the preparation of coumarins in ILs can be found in literatures. Salunkhe et. al. reported coumarin synthesis in Lewis acidic chloroaluminate IL via Pechmann condensation [15]. Unfortunately, chloroaluminate IL is moisture sensitive and very difficult to recycle after the reaction. Kumar et. al. studied the synthesis of biscoumarin derivatives in neutral IL 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim][BF_4]), which suffered from penalties of long reaction time and large amount of IL cost [16]. Therefore, if ILs posses both moisture insensitive and recyclable at the same time, it will be a potential alternative to be selected for the synthesis of coumarins.

W. Li
College of Pharmacy, Shandong University of Traditional
Chinese Medicine, Jinan 250014, People's Republic of China

Y. Wang · Z. Wang · L. Dai · Y. Wang (✉)
Shanghai Key Laboratory of Green Chemistry and Chemical
Process, Department of Chemistry, East China Normal
University, Shanghai 200062, People's Republic of China
e-mail: yywang@chem.ecnu.edu.cn

The introduction of specific functional groups has led to the identification of functionalized ionic liquids (FILs, or task specific ionic liquids, TSILs): such derivatives combine an IL-type part (in order to maintain the corresponding physical properties) with an attached extra function designed for the specific property [17–19]. The designability of the TSILs gives us more chances to manipulate the structures of them (with respect to the organic cation, inorganic anion and the length of the side chain attached to the organic cation) to achieve fitful IL of special properties according to the given reactions. Very interestingly, in our previous work [20], we discovered that change of substituents, specially a replacement of imidazolium by benzimidazolium, dramatically influences the yield and selectivity of the products in acetalization of aromatic aldehydes with diols. To extend more application of TSILs, herein, we designed and synthesized several novel SO_3H-functionalized ILs based on benzimidazolium cation (Fig. 1) to evidence their potential uses as catalysts for the synthesis of biscoumarin derivatives.

The acidity of IL is the important property relevant to its catalytic activity for acid-catalyzed reactions. In this work, the acidities of SO_3H-functionalized ILs based on benzimidazolium cation were determined using the Hammett method with UV–vis spectroscopy and their acidity–catalytic activity relationships were discussed at the molecular level according to their minimum-energy geometries determined by ab initio calculations.

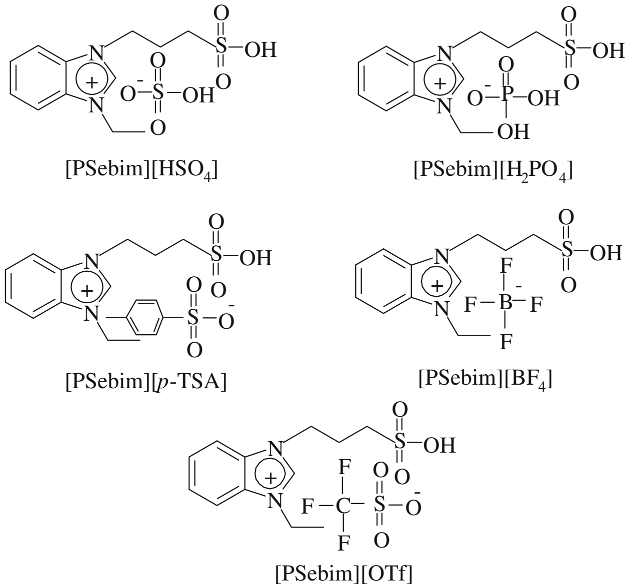

[PSebim][HSO_4]
[PSebim][H_2PO_4]
[PSebim][p-TSA]
[PSebim][BF_4]
[PSebim][OTf]

Fig. 1 Structures of SO_3H-functionalized ILs based on benzimidazolium cation

2 Experimental

2.1 Chemicals and Instruments

All chemicals involved in the experiments were analytical grade and used as received. ^1H NMR spectra were recorded on Brucker DRX-500 spectrometer. FT-IR measurements were performed using KBr disc on a NEXUS 670 FT-IR infrared spectrometer (Nicolet). UV spectra were recorded on Agilent 8453 UV–vis spectrophotometer.

2.2 Synthesis and Characterization of ILs

3-(1-Ethylbenzimidazolium-3-yl) propane-1-sulfonate (ebim-PS): Under vigorous stirring, amount of 1,3-propane sultone was dissolved in toluene, equal-mole of 1-ethylbenzimidazole was added dropwise into a round bottom flask of 25 mL capacity and maintained the temperature at 0–5 °C. After the dropping was finished, the mixture was slowly heated up to room temperature and kept for 2 h with vigorous stirring then the reaction mixture was filtered to get the white precipitate. The precipitate was washed with diethyl ether three times and dried at 100 °C for 5 h, finally giving ebim-PS as white powder.

1-Ethyl-3-(3-sulfopropyl)-benzimidazolium hydrogen sulfate ([PSebim][HSO_4]), 1-ethyl-3-(3-sulfopropyl)-benzimidazolium dihydrogen phosphate ([PSebim][H_2PO_4]), 1-ethyl-3-(3-sulfopropyl)-benzimidazolium *p*-toluenesulfonate ([PSebim][*p*-TSA]), 1-ethyl-3-(3-sulfopropyl)-benzimidazolium tetrafluoroborate ([PSebim][BF_4]), 1-ethyl-3-(3-sulfopropyl)-benzimidazolium trifluoromethanesulfonate ([PSebim][OTf]): Under vigorous stirring, amount of ebim-PS was dissolved in water and equal-mole of sulfuric acid, phosphoric acid, *p*-toluenesulfonic acid, tetrafluoroboric acid or trifluoromethanesulfonic acid was dropped slowly at room temperature. After the dropping was finished, the system was slowly heated up to 90 °C and stirred for 2 h, then the water was removed under vacuum at 70 °C for 3 h, giving [PSebim][HSO_4], [PSebim][H_2PO_4], [PSebim][*p*-TSA], [PSebim][BF_4] and [PSebim][OTf] as white powder.

[PSebim][HSO_4]: IR (KBr, ν/cm^{-1}): 3421, 3121, 3021, 2951, 2924, 2854, 1620, 1567, 1457, 1378, 1347, 1215, 1100, 708, 626, 487. ^1H NMR (500 MHz, D_2O) δ 1.57 (t, 3H, CH_3), 2.39 (m, 2H, $CH_2CH_2CH_2$), 2.95 (t, 2H, CH_2CH_3), 4.47 (m, 2H, NCH_2), 4.61 (m, 2H, CH_2SO_3H), 7.62 (m, 2H, Ph), 7.84 (m, 2H, Ph), 9.30 (s, 1H, NC*H*N). Anal. calcd. for $C_{12}H_{18}N_2S_2O_7$: C, 39.32; H, 4.95; N, 7.65; found: C, 39.25; H, 4.89; N, 7.72.

[PSebim][H_2PO_4]: IR (KBr, ν/cm^{-1}): 3426, 3124, 3021, 2954, 2930, 2859, 1623, 1567, 1442, 1378, 1346, 1216, 1193, 1008, 1092, 706, 623, 483. ^1H NMR (500 MHz,

D_2O) δ 1.57 (t, 3H, C*H*$_3$), 2.38 (m, 2H, CH_2C*H*$_2$$CH_2$), 2.95 (t, 2H, C*H*$_2$$CH_3$), 4.47 (m, 2H, NC*H*$_2$), 4.61 (m, 2H, C*H*$_2$$SO_3H$), 7.62 (m, 2H, Ph), 7.83 (m, 2H, Ph), 9.27 (s, 1H, NC*H*N). Anal. calcd. for $C_{12}H_{19}N_2O_7PS$ (366.33): C, 39.34; H, 5.23; N, 7.65; found: C, 39.28; H, 5.27; N, 7.71.

[PSebim][*p*-TSA]: IR (KBr, *ν*/cm^{-1}): 3418, 3120, 3025, 2953, 2927, 2857, 1624, 1565, 1450, 1372, 1342, 1216, 1092, 706, 621, 488. ^{1}H NMR (500 MHz, D_2O) δ 1.56 (t, 3H, C*H*$_3$), 2.02 (s, 3H, C*H*$_3$-Ph), 2.36 (m, 2H, CH_2C*H*$_2$$CH_2$), 2.92 (t, 2H, C*H*$_2$$CH_3$), 4.46 (m, 2H, NC*H*$_2$), 4.60 (m, 2H, C*H*$_2$$SO_3H$), 7.45-7.61 (m, 4H, Ph), 7.76-7.83 (m, 4H, Ph), 9.25 (s, 1H, NC*H*N). Anal. calcd. for $C_{18}H_{22}N_2O_6S_2$ (426.52): C, 50.69; H, 5.20; N, 6.57; found: C, 50.65; H, 5.24; N, 6.62.

[PSebim][BF_4]: IR (KBr, *ν*/cm^{-1}): 3439, 3126, 3017, 2995, 2929, 2862, 1630, 1413, 1378, 1342, 1219, 1087, 835, 708, 617, 491. ^{1}H NMR (500 MHz, D_2O) δ1.54 (t, 3H, C*H*$_3$), 2.37 (m, 2H, CH_2C*H*$_2$$CH_2$), 2.92 (t, 2H, C*H*$_2$$CH_3$), 4.45 (m, 2H, NC*H*$_2$), 4.62 (m, 2H, C*H*$_2$$SO_3H$), 7.62 (m, 2H, Ph), 7.84 (m, 2H, Ph), 9.27 (s, 1H, NC*H*N). Anal. calcd. for $C_{12}H_{17}N_2SO_3BF_4$: C, 40.47; H, 4.81; N, 7.87; found: C, 40.41; H, 4.79; N, 7.84.

[PSebim][OTf]: IR (KBr, *ν*/cm^{-1}): 3410, 3121, 3018, 2952, 2926, 2856, 1624, 1567, 1453, 1380, 1343, 1217, 1145, 1083, 625, 706, 487. ^{1}H NMR (500 MHz, D_2O) δ 1.54 (t, 3H, C*H*$_3$), 2.36 (m, 2H, CH_2C*H*$_2$$CH_2$), 2.92 (t, 2H, C*H*$_2$$CH_3$), 4.44 (m, 2H, NC*H*$_2$), 4.61 (m, 2H, C*H*$_2$$SO_3H$), 7.62 (m, 2H, Ph), 7.84 (m, 2H, Ph), 9.31 (s, 1H, NC*H*N). Anal. calcd. for $C_{13}H_{17}F_3N_2O_6S_2$ (418.43): C, 37.31; H, 4.10; N, 6.70; found: C, 37.27; H, 4.14; N, 6.75.

2.3 UV–Vis Acidity Evaluation

Dichloromethane solutions of the ILs were prepared with dried CH_2Cl_2 and the ILs (dried under vacuum at 70 °C for 2 h). All spectra were obtained with an Agilent B453 spectrophotometer.

2.4 General Procedure for Synthesis of Biscoumarin Derivatives

A mixture of aromatic aldehyde (20 mmol), 4-hydroxycoumarin (40 mmol) and IL (10 mol%) was added into a round bottom flask and stirred at 70 °C for the appropriate time mentioned in Tables 1 and 4. The reaction was monitored by TLC, after completion of the reaction the mixture was cooled down to room temperature. The crude solid product was extracted with diethyl ether, and then washed with water and dried over anhydrous $MgSO_4$, respectively. The IL phase, which contained some water produced in the reaction, could be easily recovered and reused in the next run after heat treatment under vacuum at 70 °C for 2 h.

2.5 Computational Methods

The minimum-energy geometries of SO_3H-functionalized ILs and isolated [PSebim]$^+$ cation were determined by performing ab initio geometry optimizations at the RHF/6-31(d, p) level using the Gaussian 03 program [22]. A vibrational analysis was performed to ensure the absence of negative frequencies and verify the existence of a true minimum.

3 Results and Discussion

3.1 Synthesis of 3,3′-Benzylidene-bis-(4-Hydroxycoumarin) Catalyzed by Various ILs

Kumar et. al. reported the synthesis of biscoumarins in large amount of neutral IL [bmim][BF_4] (Table 1, entry 1) [16]. For comparison, we investigated the synthesis of 3,3′-benzylidene-bis-(4-hydroxycoumarin) with different ILs. The results demonstrate that the catalytic performances of SO_3H-functionalized ILs based on benzimidazolium cation (Table 1, entries 3–7) are much better than that of neutral IL (Table 1, entry 2) under the same experimental conditions. On one hand, SO_3H-functionalized IL, as it behaves as an acidic catalyst, is capable of increasing the reactivity of benzaldehyde; on the other hand, the substrates have good solubility in benzimidazolium IL than imidazolium IL due to the similar structure, which facilitate the shift of the equilibrium to the aldo condensation direction. Among all SO_3H-functionalized ILs, we found that [PSebim][OTf] is the best one to catalyze the synthesis of 3,3′-benzylidene-bis-(4-hydroxycoumarin) with 95% yield.

Table 1 Synthesis of biscoumarins catalyzed by various ILs

Entry	ILs	Yield (%)[c]
1	[bmim][BF_4][a]	84
2	[bmim][BF_4][b]	63
3	[PSebim][HSO_4][b]	92
4	[PSebim][H_2PO_4][b]	81
5	[PSebim][*p*-TSA][b]	84
6	[PSebim][BF_4][b]	89
7	[PSebim][OTf][b]	95

[a] Benzaldehyde (20 mmol), 4-hydroxycoumarin (40 mmol), [bmim][BF_4] (80 mmol), $T = 70$ °C, $t = 2.0$ h [16]

[b] Benzaldehyde (20 mmol), 4-hydroxycoumarin (40 mmol), IL (10 mol%), $T = 70$ °C, $t = 2.0$ h

[c] Yield refers to isolated pure products

3.2 Determination of H_0 Values of SO_3H-Functionalized ILs

The acidic scale of these SO_3H-functionalized ILs was measured on an Agilent 8453 UV–vis spectrophotometer with a basic indicator according to the previously literature [21]. With increasing the acidic scale of the acidic ILs, the absorbance of the unprotonated form of the basic indicator decreased, whereas, the protonated form of the indicator could not be observed because of its small molar absorptivity and its location, so the $[I]/[IH^+]$ (I represents indicator) ratio could be determined from the differences of measured absorbance after the addition of Brønsted acidic ILs and Hammett function, H_0, and could be calculated by using Eq. 1. This value could be regarded as the relative acidity of the ILs.

$$H_0 = pK(I)_{aq} + \log([I]/[IH^+]) \tag{1}$$

Under the same concentration of 4-nitroanline (10 mg/L, $pk_a = 0.99$) and ILs (5 mmol/L) in dichloromethane, we determined the H_0 values of these SO_3H-functionalized ILs. The maximal absorbance of the unprotonated form of the indicator observed in CH_2Cl_2 was 350 nm. Up on the addition of IL, the absorbance of the unprotonated form of the basic indicator decreased.

As shown in Fig. 2, the absorbance of the unprotonated form of the indicator on five TSILs decreased as following order: $[PSebim][H_2PO_4] > [PSebim][p\text{-}TSA] > [PSebim][BF_4] > [PSebim][HSO_4] > [PSebim][OTf]$. After the calculation, we obtained the acidity order of the nine ILs with the following H_0 values (Table 2): [PSebim][OTf] (−0.09) > $[PSebim][HSO_4]$ (0.05) > $[PSebim][BF_4]$ (0.19) > [PSebim][*p*-TSA] (0.42) > $[PSebim][H_2PO_4]$ (0.64), which is consistent with the sequence of catalytic activity observed in the synthesis of biscoumarin derivatives. The acidities of the ILs depended both on the characteristics of the cations and anions. When the cations of the ILs were the same, the acidities of the ILs significantly depended on anions. And the acidities of the ILs with the conjugate base of $[OTf]^-$ as the anion reached the highest (Table 2, entry 6).

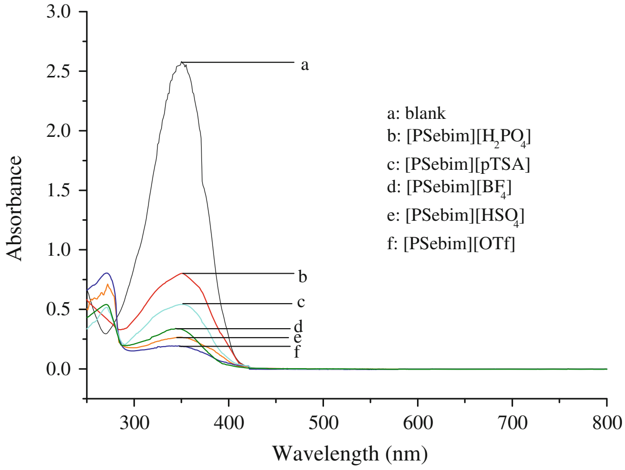


Fig. 2 Absorbance spectra of 4-nitroaniline for various SO_3H-functionalized ILs in CH_2Cl_2

3.3 The Molecular Geometries of TSILs

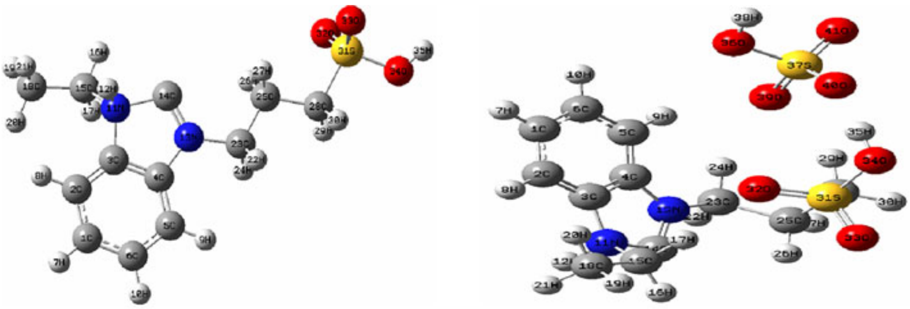
The minimum-energy geometries of TSILs were determined by performing ab initio geometry optimizations at the RHF/6-31(d, p) level. The fully optimized geometries of these ILs are presented in Fig. 3; Table 3. It is obvious that a strong hydrogen bond network is presented in the SO_3H-functionalized ILs. Taking IL $[PSebim][HSO_4]$ for example, the anion is located on the side of the propyl sulfonic acid group, and interacts with the propyl alkyl sulfonic acid group and benzimidazolium ring in the form of C–H···O or O–H···O(F) type (hydrogen bonds). There are six hydrogen bonds in IL $[PSebim][HSO_4]$, which are shorter than the Van der Waals distance of 2.67 Å [23]. These include the hydrogen bonds $C_5–H_9\cdots O_{39}$ (bond distance is 2.2421 Å) between the anion and benzimidazolium ring; the hydrogen bonds $C_{23}–H_{24}\cdots O_{39}$, $C_{28}–H_{29}\cdots O_{39}$ (bond distances are 2.4129, 2.2738 Å) between the anion and alkyl sulfonic acid chain; the hydrogen bond $C_{15}–H_{17}\cdots O_{32}$ (bond distance is 2.3301 Å) between benzimidazolium ring and alkyl sulfonic acid chain; the hydrogen bond $C_{28}–H_{29}\cdots O_{34}$ (bond distance is 2.6615 Å) inside the alkyl sulfonic acid chain; the most importantly, the strongest interaction between the anion and the sulfonic acid proton was $O_{34}–H_{35}\cdots O_{40}$ (bond distance is 1.6459 Å). The other four SO_3H-functionalized ILs also exhibit similar strong interactions between the anions and the sulfonic acid groups, which make the H–O bond of the sulfonic acid group to be lengthened with different levels compared with that of in the isolated cation. When the cations of the ILs are the same, the H–O bond distance of SO_3H-functionalized ILs decreased as following

Table 2 Calculation and comparison of H_0 values of different SO_3H-functionalized ILs in CH_2Cl_2

Entry	ILs	A_{max}	[I](%)	$[IH^+]$(%)	H_0
1	–	2.546	100.0	0	–
2	$[PSebim][HSO_4]$	0.266	10.4	89.6	0.05
3	$[PSebim][H_2PO_4]$	0.793	31.1	68.9	0.64
4	[PSebim][*p*-TSA]	0.538	21.1	78.9	0.42
5	$[PSebim][BF_4]$	0.336	13.2	82.6	0.19
6	[PSebim][OTf]	0.193	7.6	92.4	−0.09

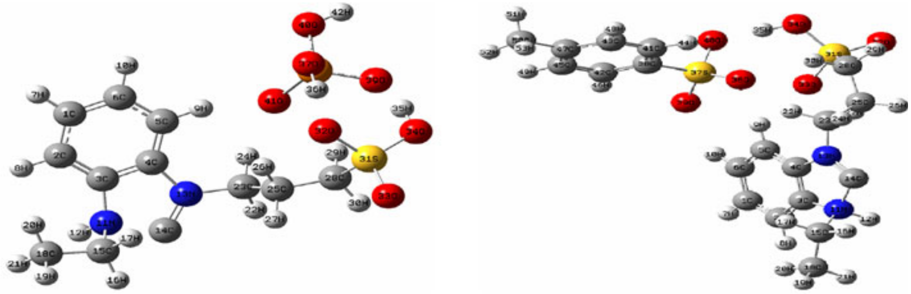
Indicator 4-nitroaniline

Fig. 3 Molecular structures of isolated $[PSebim]^+$ cation and ILs based on $[PSebim]^+$ cation



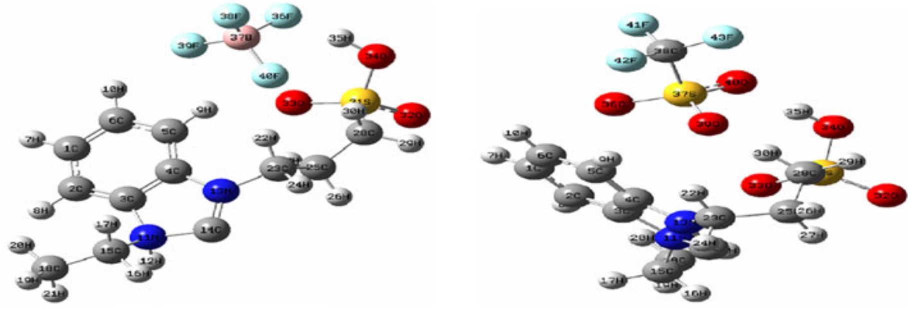
$[PSebim]^+$

$[PSebim][HSO_4]$



$[PSTma][H_2PO_4]$

[PSMim][*p*-TSA]



$[PSTma][BF_4]$

[PSTma][OTf]

Table 3 The geometry parameters of isolated cations and SO_3H-functionalized ILs

	Cation	$[PSebim][HSO_4]$	$[PSebim][H_2PO_4]$	[PSebim][*p*-TSA]	$[PSebim][BF_4]$	[PSebim][OTf]
H–O bond distance (Å)	$H_{35}–O_{34} = 0.9491$	$H_{35}–O_{34} = 0.9784$	$H_{35}–O_{34} = 0.9936$	$H_{35}–O_{34} = 0.9903$	$H_{35}–O_{34} = 0.9844$	$H_{35}–O_{34} = 0.9702$
Distance between the anion and sulfonic acid group (Å)		$H_{35}\cdots O_{40} = 1.6459$	$H_{35}\cdots O_{40} = 1.2937$	$H_{35}\cdots O_{40} = 1.4478$	$H_{35}\cdots F_{36} = 1.5362$ $H_{35}\cdots F_{40} = 2.5300$	$H_{35}\cdots O_{40} = 1.6946$
Other hydrogen bonds in ILs (Å)		$H_{17}\cdots O_{32} = 2.3301$ $H_{24}\cdots O_{39} = 2.4129$ $H_{29}\cdots O_{34} = 2.6615$ $H_{29}\cdots O_{39} = 2.2738$ $H_9\cdots O_{39} = 2.2421$	$H_{36}\cdots O_{32} = 1.3757$ $H_9\cdots O_{41} = 1.8727$ $H_{24}\cdots O_{41} = 2.1107$ $H_{25}\cdots O_{32} = 2.2638$	$H_{30}\cdots O_{36} = 2.1878$ $H_{22}\cdots O_{36} = 2.0690$ $H_9\cdots O_{36} = 2.2778$ $H_{10}\cdots O_{39} = 2.4514$	$H_{30}\cdots F_{40} = 2.1851$ $H_9\cdots F_{40} = 2.0386$ $H_{22}\cdots F_{40} = 2.1424$ $H_{10}\cdots F_{39} = 2.4253$	$H_{30}\cdots O_{39} = 1.7740$ $H_{22}\cdots O_{39} = 2.4436$ $H_9\cdots O_{39} = 2.4700$ $H_{10}\cdots O_{36} = 2.2382$

order: $[PSebim][H_2PO_4]$ ($H_{35}–O_{34} = 0.9936$) > [PSebim] [*p*-TSA] ($H_{35}–O_{34} = 0.9903$) > $[PSebim][BF_4]$ ($H_{35}–O_{34}= 0.9844$) > $[PSebim][HSO_4]$ ($H_{35}–O_{34} = 0.9784$) > [PSebim][OTf] ($H_{35}–O_{34} = 0.9702$), which is contrary to their acidity sequence. The formation of hydrogen bond was a process of sharing lone electron pair of O or F atom

Table 4 Synthesis of various biscoumarin derivatives catalyzed by IL [PSebim][OTf]

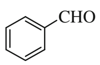
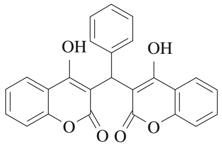
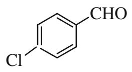
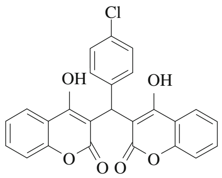
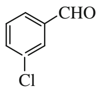
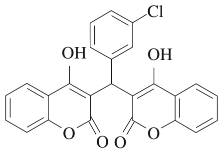
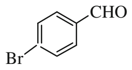
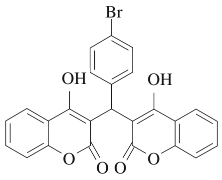
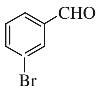
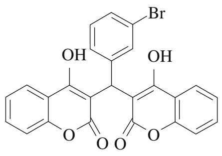
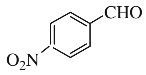
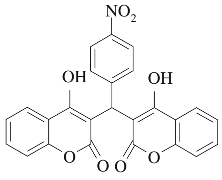
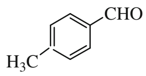
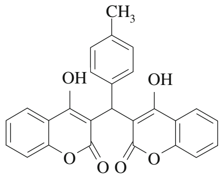
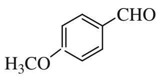
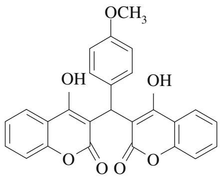
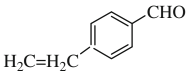
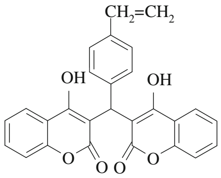
Entry	Substrate	Product	Time (h)	Yield (%)[a]
1			2.0	95
2			2.0	96
3			2.0	94
4			2.0	95
5			2.0	94
6			2.0	96
7			2.5	93
8			2.5	93

Table 4 continued

Entry	Substrate	Product	Time (h)	Yield (%)[a]
9			3.0	92

[a] Yield refers to isolated pure products: aromatic aldehyde (20 mmol), 4-hydroxycoumarin (40 mmol), IL (10 mol%), $T = 70$ °C

with H atom. When the hydrogen bond was strong, the lone electron pair was shared in deep degree, and cause an increase in the electron density and stability of H atom. As a result, the acidity of H atom decreased.

3.4 The Generality of SO_3H-Functionalized ILs Towards the Synthesis of Various Biscoumarin Derivatives

The generality of the SO_3H-functionalized ILs to the various aromatic aldehydes was investigated in Table 4, in which different functional groups such as Cl, Br, NO_2, Me, OMe were selected to react with 4-hydroxycoumarin in the presence of 10 mol% of IL [PSebim][OTf]. The reactivities of aromatic aldehydes with electron donating (entries 7–9, Table 4) as well as with electron withdrawing groups (entries 2–6, Table 4) are almost the same with biscoumarins in good to excellent yields. Effect of substitute position (entries 2–5, Table 4) on the reactivity of aryl ring is not significant.

3.5 Reusability of [PSebim][OTf] as Catalyst for the Synthesis of 3,3′-Benzylidene-Bis-(4-Hydroxycoumarin)

Compared with traditional acid catalysts, easy recycling is an attractive property of the TSILs. Consequently, we investigated the catalytic activity of recycled IL [PSebim][OTf] in the synthesis of 3,3′-benzylidene-bis-(4-hydroxycoumarin). Upon completion in each run, the reaction solution was cooled to room temperature. The substrates and the products were extracted with diethyl ether. The left IL phase contained some H_2O which make it recovery easily and can be used directly without further treatment. It was found that IL [PSebim][OTf] with some H_2O can be reused for at least two subsequent reactions without significant loss of activity, however, for the next four runs, it showed lower efficiency in terms of products yields (Table 5). On the other hand, if the formed byproduct H_2O was removed at 70 °C upon completion in each run, the activity of [PSebim][OTf] maintained even better. After six runs, no obvious loss of catalytic activity was observed as shown in Table 5. This indicated that the IL [PSebim][OTf] was a high efficient and recyclable catalyst for aldo condensation of 4-hydroxycoumarin with 4-nitrobenzaldehyde.

Table 5 Recycling of the IL [PSebim][OTf]

Recycling times	Yield (%)[a]/H_2O was removed	Yield (%)[a]/H_2O was accumulated
1	95	92
2	93	87
3	93	84
4	92	82
5	92	81
6	91	78

[a] Yield refers to isolated pure products: Benzaldehyde (20 mmol), 4-hydroxycoumarin (40 mmol), [PSebim][OTf] (10 mol%), $T = 70$ °C, $t = 2.0$ h

3.6 Plausible Mechanism for the Catalytic Activity of SO_3H-Functionalized ILs

The plausible reaction mechanism for the synthesis of biscoumarin derivatives is expected to follow the general scheme shown in Fig. 4. Aldo condensation of 4-hydroxycoumarin with aromatic aldehyde under mild condition can proceed by the acid-catalyzed mechanism. SO_3H-functionalized ILs is capable of binding with the carbonyl oxygen increasing the reactivities of parent carbonyl as it behaves as a acidic catalyst. As shown in Fig. 4, first IL activates carbonyl group of aromatic aldehyde to give IL-aldehyde complex I and thus increases the electrophilicity carbonyl carbon of aldehyde. Nuleophilic addition of 4-hydroxycoumarin to I to give II and followed by loss of H_2O from II to afford III, which is further activated by acidic IL. Another molecule of 4-hydroxycoumarin is

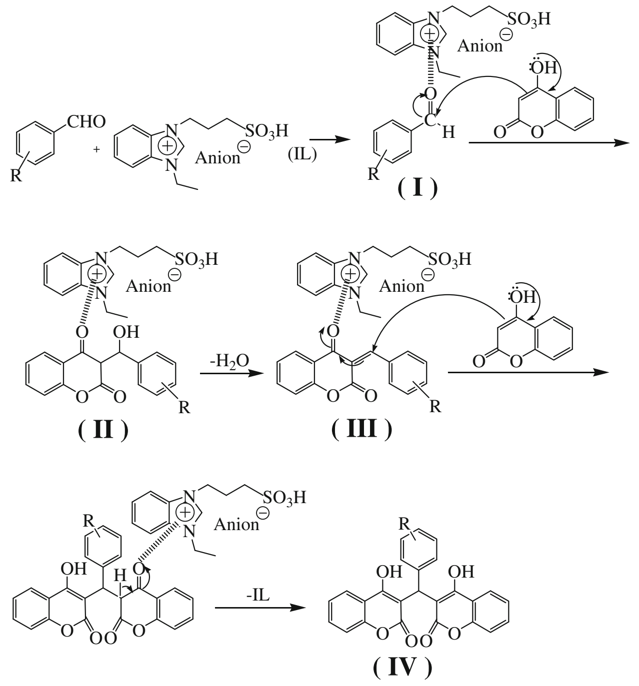


Fig. 4 Plausible mechanism for the catalytic activity of SO_3H-functionalized IL

added to III to give IV and IL, which can catalyze reaction in a catalytic manner.

4 Conclusion

In conclusion, the present procedure using easily available novel SO_3H-functionalized ILs based on benzimidazolium cation provides a very simple and efficient methodology for the synthesis of biscoumarin derivatives by a one-pot condensation of 4-hydroxycoumarin with aromatic aldehydes. Furthermore, this series of SO_3H-functionalized ILs have higher catalytic activities under mild reaction condition without the addition of any other organic solvents or catalysts. The results got from the experiments and the minimum-energy geometries of SO_3H-functionalized ILs revealed that the acidities and catalytic activities of ILs in aldo condensation were related to their structures. The IL with shorter H–O bond distance has stronger acidity and higher catalytic activity in the synthesis of biscoumarin derivatives.

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