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A novel nano perfluoro ionic liquid as an efficient catalyst in the synthesis of chromenes under mild and solvent-free conditions

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ABSTRACT

1-Methyl-1*H*-imidazol-3-ium 2,3,4,5,6-pentafluorophenolate [mim]C_6F_5O as a novel nano ionic liquid was designed, synthesized and characterized by using various techniques such as Fourier transform spectroscopy infrared (FT-IR), nuclear magnetic resonance (NMR), x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy (EDX), thermal gravimetric analysis (TGA), derivative thermal gravimetric (DTG) and elemental analysis (CHN). The described nano perfluoro ionic liquid was used as an efficient catalyst in the synthesis of 2-amino-4,5-dihydropyrano[3,2-*c*]chromene, 3-amino-1*H*-benzo[*f*]chromene and 2-amino-4*H*-chromene derivatives under mild and solvent-free conditions. Short reaction times, good yields of products, easy work-up are the major advantages of this work.

Keywords: *Nano perfluoro ionic liquid, [mim]C_6F_5O, 1-Methyl-1H-imidazol-3-ium-2,3,4,5,6-pentafluorophenolate, Chromenes, Solvent-free conditions.*

1. Introduction

Nowadays, developed and developing countries wish to introduce pollution prevention strategies for reduction and management of chemical industries wastes. With this aim, development of fluorous chemistry is more attractive for fluorine chemists because the application of perfluoro solvents and/or catalysts will reduce heating/energy costs and lead to a net reduction in global warming from fossil carbon sources. Over the last decades, many novel catalysts with excellent affinities for fluorous solvents have been reported [1]. A literature survey will be shown that catalysts which are perfluoro tags within their molecular structures can be easily separated from reaction mixture using perfluoro solvents [2]. Considering this aim, we wish to report a novel nano ionic liquid (NIL) with a perfluoro anionic tag in this article.

Organic multi-component reactions (MCRs) are important than traditional ones because they have ability of target compounds preparation with better atomic economy and efficiency [3].

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To the best of our knowledge, the increased catalyst's surface will increase the contact between catalyst and reactant [4-6]. The molten salts (MSs), lately named as ionic liquids (ILs), are salts melting point of which is below 100 °C [7]. These ILs can be used as the catalyst and solvent in organic synthesis, extraction and electrochemistry etc. because of their unique properties such as non-flammability, the ability to dissolve a wide range of materials, low volatility, negligible vapor pressure, and high thermal stability. For example, in liquid–liquid extraction processes, Ionic-liquids can be used as good receptors for metallic radioactive species [8]. Metal-free organic catalyst termed as the organo catalyst are more suitable than transition metal catalysts in the production of pharmaceutical intermediates. Ionic liquids (ILs) can be also considered as organo catalysts [9]. On the other hand, performance of reactions under solvent-free conditions is one of green chemistry protocols that have advantages such as short reaction times, good yields of products, easier work up and harmful organic solvents removal [10].

Chromenes are important organic molecules which have a wide range of applications in various fields of chemistry, pharmacology and biology. Chromene derivatives have been used as bioactive molecules such as antitumor [11], cytotoxicity [12], antifungal [13],

anticancer [14], molluscicidal [15], antihyperglycemic agents [16] and anti-inflammatory [17]. Moreover, they have been also employed as intermediates in the synthesis of organic and natural products [18].

In continuation of our research on the application of Nafion-*H* as an excellent thermal and mechanical stable perfluorinated resin [19], herein, we wish to report the design, synthesis and application of 1-methyl-1*H*-imidazol-3-ium 2,3,4,5,6-pentafluorophenolate [mim]C_6F_5O as a novel nano ionic liquid (Scheme 1).

The described [mim]C_6F_5O was fully characterized using FT-IR, ^{1}H and ^{13}CNMR, XRD, SEM, TEM, EDX, TGA, DTG and CHN. Then, it was employed as a highly efficient and recyclable nano catalyst in the synthesis of chromenes *via* one-pot multi-component condensation of arylaldehydes, malononitrile and one of the 4-hydroxycoumarin, *β*-naphtol and resorcinol, under mild and solvent-free conditions (Scheme 2).

2. Experimental

2.1. General

All chemicals were purchased from Merck chemical company. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. The ^{1}H NMR (300 or 400 MHz) and ^{13}C NMR (75 or 100 MHz) were run on a Bruker Avance DPX FT-NMR spectrometer (δ in ppm). The crystal structure of synthesized materials was determined by an X-ray diffractometer (Italstructure ADP2000 XRD diffractometer) at ambient temperature. Thermal gravimetric analysis (TGA) and differential thermal gravimetric (DTG) were analyzed by a PerkinElmer (Model: Pyris 1). TG/DTG analysis include 25–600 °C, temperature increase rate of 10 °C min^{-1}, Nitrogen atmosphere.

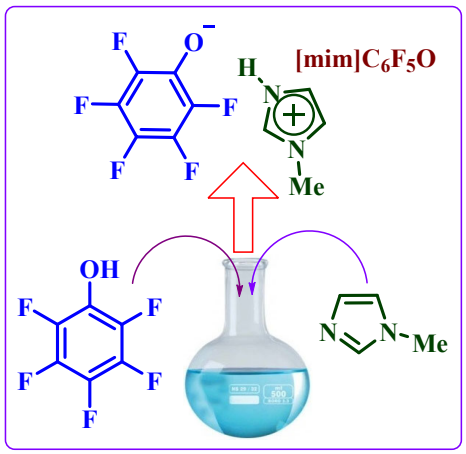
2.2. Catalyst preparation

1-Methylimidazole (10 mmol, 0.85 g) was added drop wise to the stirred pentafluorophenol (10 mmol, 1.84 g) at room temperature over a period of 5 min, and the resulting solid was triturated with *n*-hexane (2 × 10 mL). Then resulted ionic liquid being dried under vacuum at 50 °C to give [mim]C_6F_5O as a cream solid in 94 % yield (2.50 g).

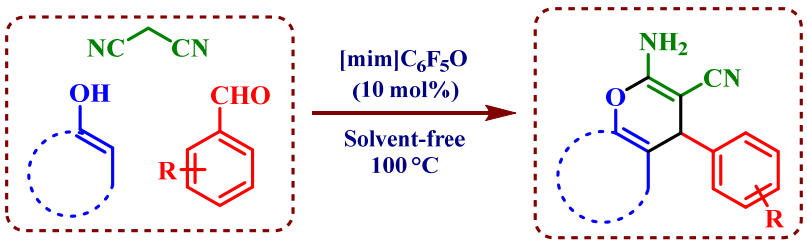
Cream solid. m.p.= 62-64°C; IR (KBr): $\bar{\nu}$ = 749, 835, 990, 1147, 1502, 3155 cm^{-1}. ^{1}HNMR (300 MHz, DMSO-d_6): δ= 3.70 (s, 3H), 7.05 (s, 1H), 7.24 (s, 1H), 7.45 (s, 1H), 7.92 (s, 1H) ppm. ^{13}CNMR (75 MHz, DMSO-d_6): δ= 33.8, 121.6, 126.0, 130.3, 133.5, 136.2, 136.4, 136.6, 137.6, 139.6, 139.8, 140.9 ppm. MS: *m/z*= 267 $[M+H]^+$, 266 $[M]^+$. CHN Analysis: Anal. Calcd for $C_{10}H_7F_5N_2O$: C, 45.12; H, 2.65; F, 35.69; N, 10.52; O, 6.01; Found: C, 44.84; H, 2.50; N, 9.38.

2.3. General procedure for the synthesis of chromene derivatives using [mim]C_6F_5O

To a mixture of 4-hydroxycoumarin or *β*-naphtol or resorcinol (1 mmol), malononitrile (1 mmol), aldehyde (1mmol) and [mim]C_6F_5O (0.026 g, 0.1 mmol, 10 mol%) in a 10 mL round-bottomed flask connected to a reflux condenser was stirred in an oil-bath at 100 °C. The reaction was monitored by TLC. After completion of the reaction, the catalyst was extracted by warm water (10 mL) from the reaction mixture.



Scheme 1. Preparation of 1-methyl-1*H*-imidazol-3-ium 2,3,4,5,6-pentafluorophenolate [mim]C_6F_5O as a novel nano perfluoro ionic liquid catalyst.



Scheme 2. Synthesis of chromenes using [mim]C_6F_5O as nano perfluoro ionic liquid.

The catalyst was soluble in warm water and separated from the target products. The solid residue was purified by washing with ethanol and crystallized from hot ethanol to give the desired product. Finally, the aqueous filtrate containing [mim]C_6F_5O was distilled and the solid residue was dried under reduced pressure, weighed and reused to investigate the recyclability of the catalyst. A 0.1 M solution of pentafluorophenol and its corresponding IL were prepared and their pH was measured. It was found that pH of pentafluorophenol and IL are 3.40 and 5.80, respectively.

Selected spectral data

2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile ***(1)****:*

IR (KBr): $\bar{\nu}$ = 3381, 2198, 1709, 1675, 1605, 1380, 1057, 758 cm^{-1}. ^{1}HNMR (400 MHz, DMSO-d_6): δ= 4.46 (s, 1H), 7.25 (m, 3H), 7.32 (m, 2H), 7.40 (d, 2H), 7.49 (m, 2H), 7.72 (m, 1H), 7.91 (dd, 1H) ppm. ^{13}CNMR (100 MHz, DMSO-d_6): δ= 36.9, 57.9, 103.9, 112.9, 116.5, 119.2, 122.4, 124.6, 127.0,127.6, 128.4, 132.9, 143.3, 152.1, 153.3, 157.9, 159.5 ppm.

2-amino-4-(4-chlorophenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile ***(4)****:*

IR (KBr): $\bar{\nu}$ = 3382, 2193, 1713,1676, 1610, 1377, 1061, 759 cm^{-1}. ^{1}HNMR (400 MHz, DMSO-d_6): δ= 4.65 (s, 1H), 7.47 (d, 2H), 7.53 (d, 2H), 7.62 (m, 2H), 7.67 (d, 2H), 7.88 (m, 1H), 8.05 (d, 1H) ppm. ^{13}CNMR (100 MHz, DMSO-d_6): δ= 36.3, 57.4, 103.4, 112.9, 116.5, 119.0, 122.4, 124.6, 128.4, 129.6, 131.6, 132.9, 142.3, 152.1, 153.5, 157.8, 159.5 ppm.

2-amino-4-(4-hydroxyphenyl)-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile ***(5)****:*

IR (KBr): $\bar{\nu}$ = 3504, 3408, 2197, 1696, 1610, 1380, 1172, 760 cm^{-1}. ^{1}HNMR (400 MHz, DMSO-d_6): δ= 4.39 (s, 1H), 6.75 (m, 2H), 7.11 (m, 2H), 7.41 (s, 2H), 7.54 (m, 2H), 7.76 (m, 1H), 7.95 (dd, 1H), 9.42 (s, 1H) ppm. ^{13}CNMR (100 MHz, DMSO-d_6): δ= 36.11, 58.3, 104.4, 112.9, 115.14, 116.5, 119.3, 122.3, 124.6, 128.6, 132.7, 133.6, 152.0, 152.9, 156.4, 157.8, 159.5 ppm.

3. Results and Discussion

3.1. Characterization of [mim]C_6F_5O

The structure of [mim]C_6F_5O was identified using various techniques such as FT-IR, ^{1}HNMR, ^{13}CNMR, XRD, SEM, TEM, EDX, CHN, TGA and DTG.

The FT-IR spectrum of the novel nanostructured ionic liquid showed a broad peak at 3155 cm^{-1} which could be related to the N-H stretching group on the imidazolium ring (Fig. 1).

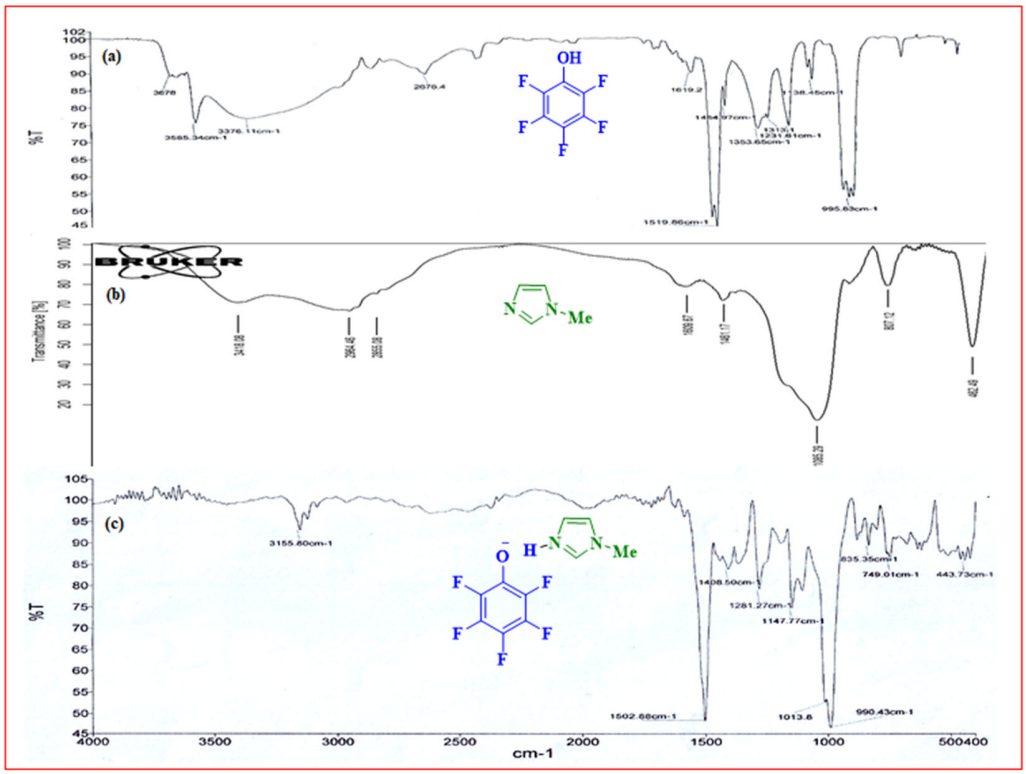


Fig. 1. FT-IR spectrum of pentafluorophenol (a); 1-methylimidazole (b); 1-methyl-1*H*-imidazol-3-ium- 2,3,4,5,6-pentafluorophenolate ([mim]C_6F_5O) (c).

Moreover, the ^{1}HNMR and ^{13}CNMR spectra of [mim]C_6F_5O were investigated (shown in Fig. 2 and 3). As shown in Fig. 2, the peak at δ = 7.46 was related to the acidic hydrogen of the N-H group. The peak appeared at 2.51 ppm is related to the methyl group.

The TGA and DTG analyses of 1-methyl-1*H*-imidazol-3-ium 2,3,4,5,6-pentafluorophenolate were also studied. The related diagrams are shown in Fig. 4. As can be seen in these diagrams, the important weight loss and decomposing occur in one step, after 150 °C.

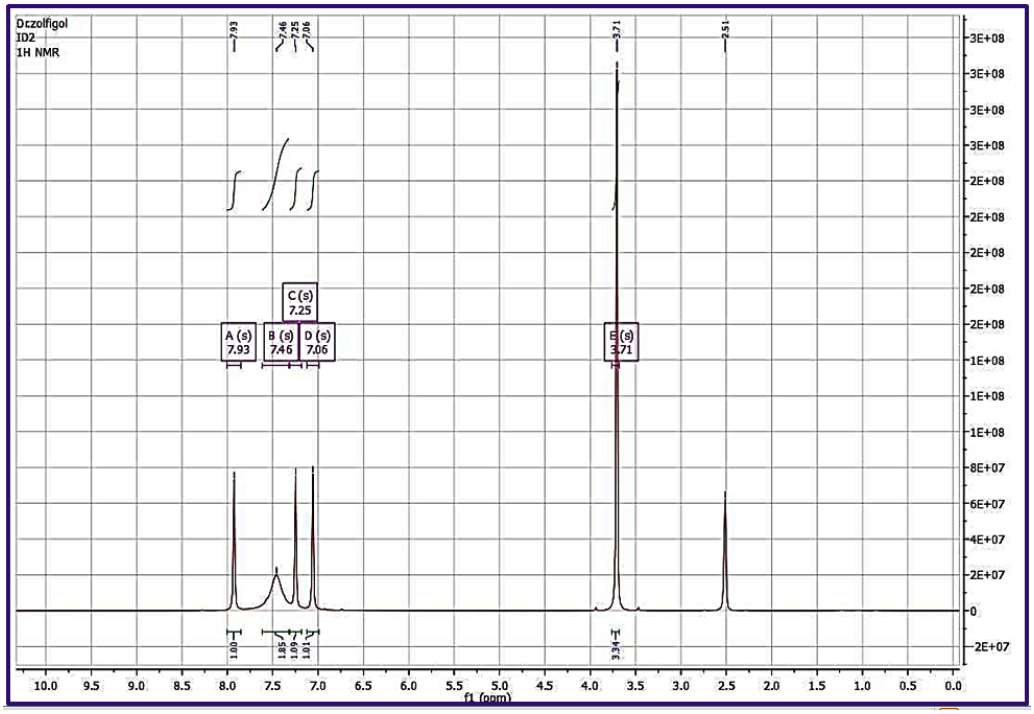


Fig. 2. ^{1}HNMR spectrum of [mim]C_6F_5O as a novel nano perfluoro ionic liquid.

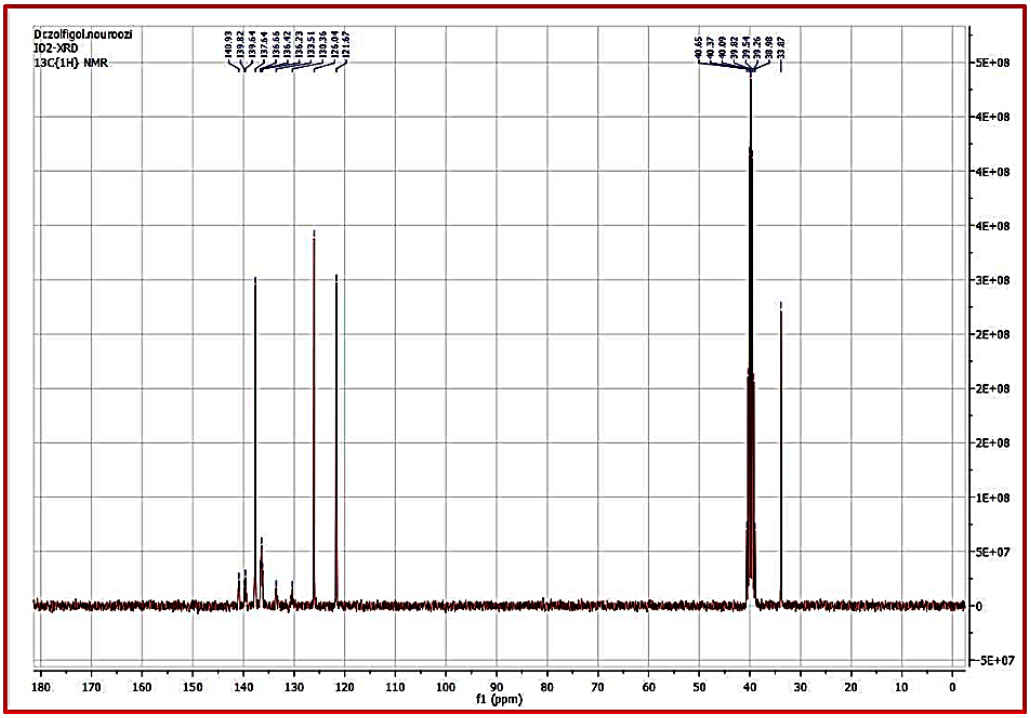


Fig. 3. ^{13}CNMR spectrum of [mim]C_6F_5O as a novel nano perfluoro ionic liquid.

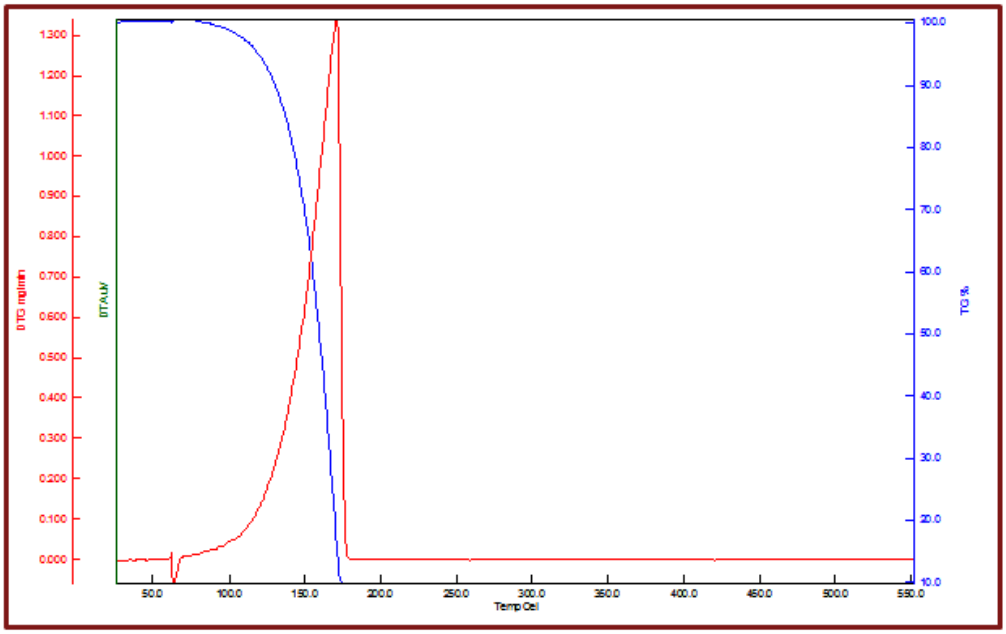


Fig. 4. Thermal gravimetric (TGA) and derivative thermal gravimetric (DTG) of [mim]C_6F_5O.

Energy-dispersive x-ray spectroscopy (EDX) of the nano ionic liquid confirmed the presence of the expected elements in its structure such as carbon, oxygen, nitrogen and fluorine (Fig. 5).

X-ray diffraction analysis (XRD) pattern of [mim]C_6F_5O was in the domain of 2–90°. As presented in Fig. 6, XRD patterns exhibited diffraction lines of a high crystalline nature at about 2θ≈ 14.60° and 27.10°.

As shown in Table 1, the peak width (FWHM), size and inter planer distance for the XRD pattern of [mim]C_6F_5O were studied in the range of 14.60° to 27.10°. Using Debye–Scherrer formula (D= Kλ/(βcosθ)) [20], the average size of particles was investigated. According to the above mentioned formula, the size of particles was found to be in the nanometer range (17.04 to 30.27 nm), which was in close agreement with those recorded by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figs. 7 and 8).

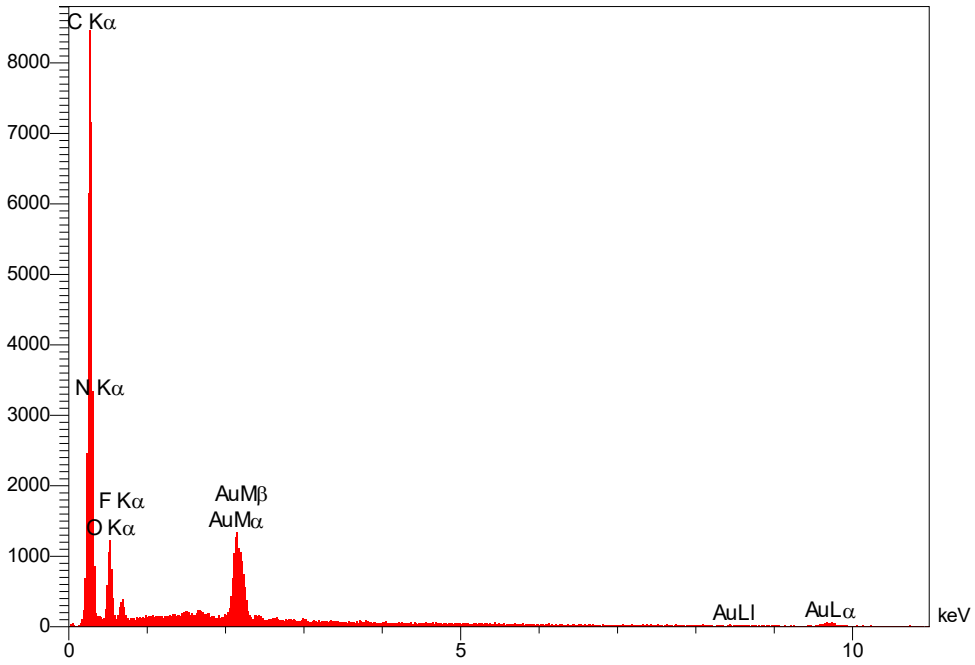


Fig. 5. Energy-dispersive x-ray spectroscopy (EDX) of [mim]C_6F_5O.

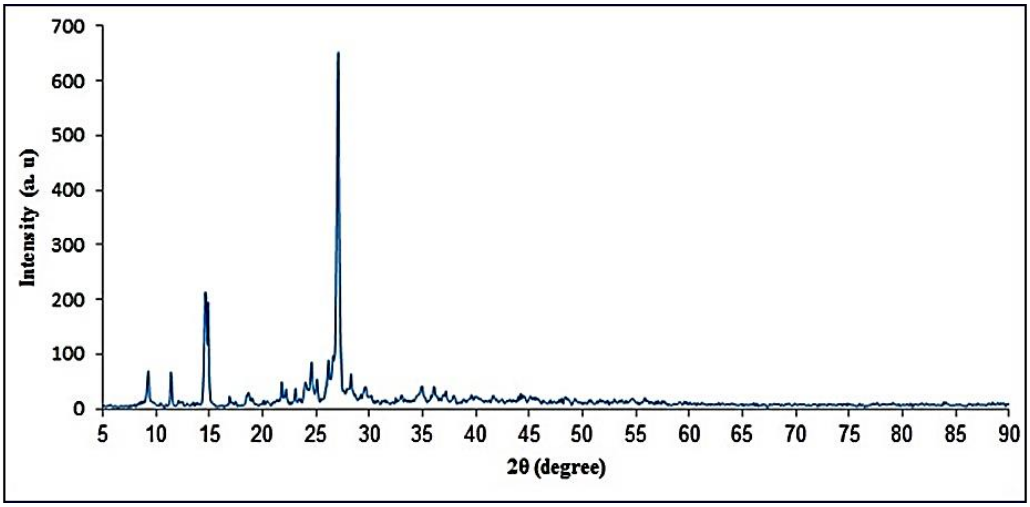


Fig. 6. X-ray diffraction analysis (XRD) pattern of [mim]C_6F_5O.

Table 1. X-ray diffraction (XRD) data for 1-methyl-1*H*-imidazol-3-ium 2,3,4,5,6-pentafluorophenolate.

Entry	2θ	Peak width [FWHM] (degree)	Size [nm]	Inter planer distance [nm]
1	14.60	0.47	17.04	0.60
2	27.10	0.27	30.27	0.33

To confirm the difference between catalysts, 1-methylimidazole and pentafluorophenol, their UV/Vis absorbance spectra were also compared. As shown in Fig. 9, in the UV/Vis spectra of 1-methylimidazole and pentafluorophenol, λ_{max} appeared at about 275 and 267, but in the UV/Vis spectrum of [mim]C_6F_5O, the λ_{max} value was depicted at about 262 nm.

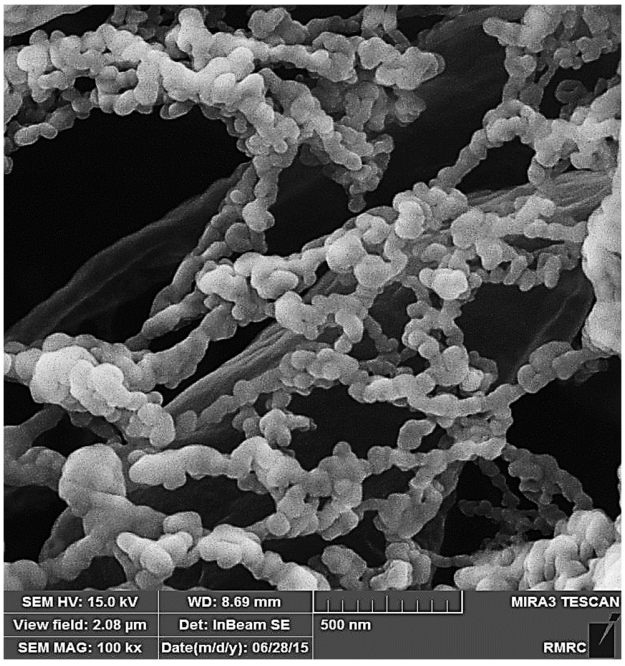


Fig. 7. Scanning electron microscopy (SEM) of [mim]C_6F_5O.

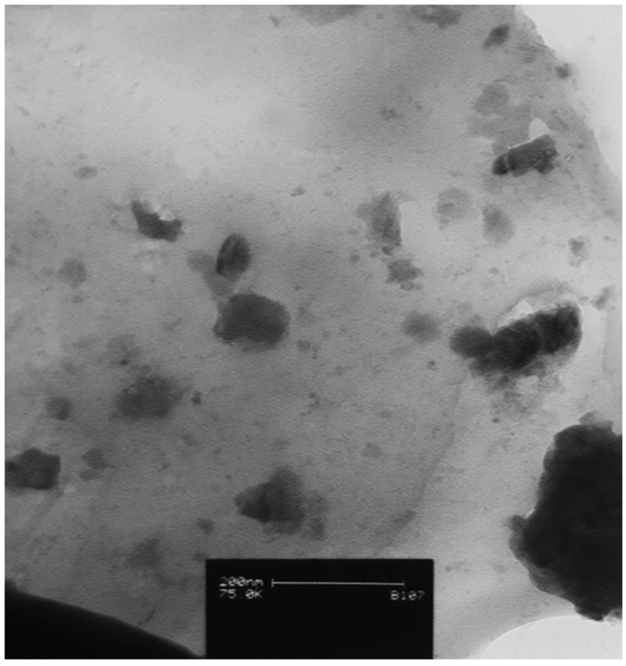


Fig. 8. Transmission electron microscopy (TEM) of nano perfluoro ionic liquid [mim]C_6F_5O.

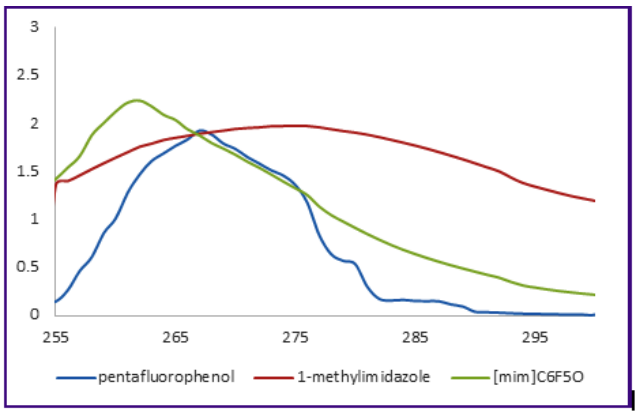


Fig. 9. UV/Vis absorbance spectra of nano ionic liquid [mim]C_6F_5O.

3.2. Activity of [mim]C_6F_5O as a task-specific nano ionic liquid catalyst

After characterization of [mim]C_6F_5O, we have investigated its catalytic activity in the synthesis of chromenes. To optimize the reaction conditions, condensation of 4-hydroxycoumarin (0.162 g, 1 mmol), malononitrile (0.066 g, 1 mmol) and benzaldehyde (0.106 g, 1 mmol) was selected as the model reaction. The reaction mixture was stirred in the presence of different amounts of catalyst at the range of 25- 110 °C under solvent-free conditions (Table 2). As shown in Table 2, 10 mol% of [mim]C_6F_5O (0.026 g), at 100 °C is an appropriate condition to catalyze the reaction.

The solvent effect on the condensation of 4-hydroxycoumarin (1 mmol), malononitrile (1 mmol) and benzaldehyde (1 mmol) in the presence of 10 mol% of [mim]C_6F_5O was investigated and the results were compared to those with the solvent-free condition. As illustrated in Table 3, the solvent-free condition was the best choice.

To study of the catalyst ability, various chromenes were synthesized by the condensation reaction of a wide range of aromatic aldehydes, malononitrile and one of the 4-hydroxycoumarin, *β*-naphtol and/or resorcinol. The results are shown in Table 4.

Table 2. The reaction of 4-hydroxycoumarin, benzaldehyde and malononitrile using different amounts of [mim]C_6F_5O and temperature.

Entry	Mol% of Catalyst	Temp. (°C)	Time (min)	Yield (%)[a]
1	5	100	15	90
2	7	100	10	90
3	**10**	**100**	**5**	**96**
4	15	100	5	96
5	10	25	30	40
6	10	50	30	70
7	10	80	20	92
8	10	110	5	96

[a]Isolated yield.

Table 3. The reaction of 4-hydroxyoumarin, benzaldehyde and malononitrile in different solvent in the presence of 10 mol% of [mim]C_6F_5O.

Entry	Solvent	Temp. (°C)	Time (min)	Yield (%)[a]
1	H_2O	Reflux	75	95
2	EtOH	Reflux	50	54
3	CH_3CN	Reflux	60	40
4	EtOAc	Reflux	80	30
5	Solvent-free	100	5	96

[a]Isolated yield.

Table 4. Solvent-free synthesis of chromene derivatives catalyzed by [mim]C_6F_5O at 100 °C.

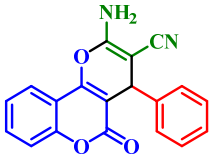
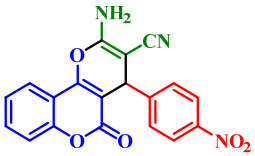
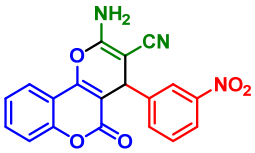
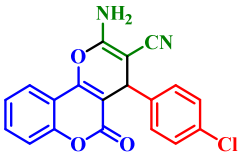
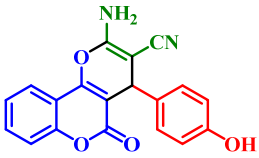
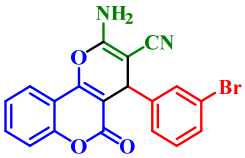
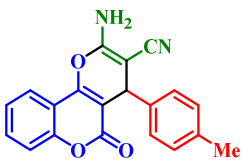
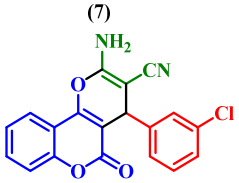
Structures	Time (min)	Yield (%)	m.p. (°C)		Ref.
			Found	Reported	
	5	96	262-264	258-260	[21]
(1) 	5	85	256-258	255-257	[21]
(2) 	8	91	260-262	260-262	[21]
(3) 	5	91	267-269	263-265	[21]
(4) 	5	96	263-265	260-263	[21]
(5) 	5	94	275-277	276-278	[22]
(6) 	8	98	255-257	253-255	[22]
(7) 	10	97	244-246	241-243	[23]
(8)					

Table 4. *(Continued)*

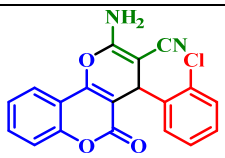
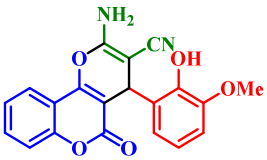
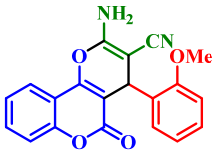
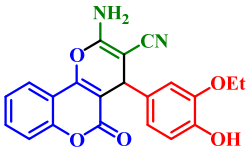
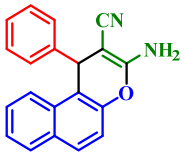
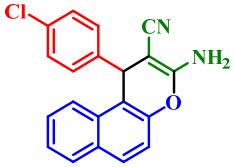
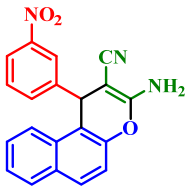
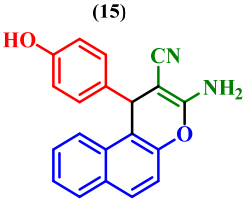
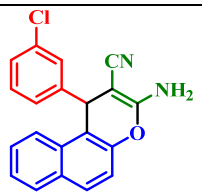
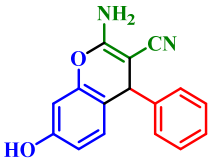
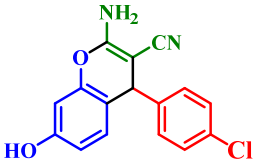
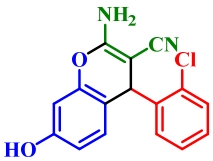
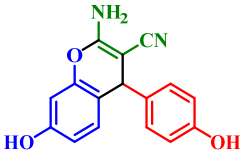
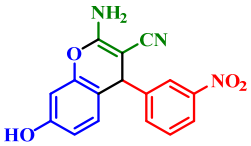
 (9)	8	99	277-279	275-277	[21]
 (10)	5	94	183-185	180-182	[24]
 (11)	8	93	233-235	234-237	[25]
 (12)	10	93	242-244	248-250	[26]
 (13)	8	85	281-283	278-279	[27]
 (14)	10	95	215-216	206-208	[28]
 (15)	8	95	233-235	232-234	[29]
 (16)	10	78	199-201	200-202	[30]

Table 4. *(Continued)*

 (17)	10	82	237-239	239-240	[29]
 (18)	20	85	233-235	232-234	[27]
 (19)	15	80	161-163	162-164	[31]
 (20)	15	70	237-239	239-240	[29]
 (21)	15	73	263-265	248-250	[32]
 (22)	12	80	171-173	189-191	[31]

Recyclability is an important advantage of any catalyst, so recyclability of [mim]C_6F_5O was also investigated. For this purpose, the multicomponent reaction of 4-hydroxycoumarin (1 mmol), benzaldehyde (1 mmol) and malononitrile (1 mmol), in presence of catalytic amount of [mim]C_6F_5O at 100 °C was performed. Upon completion of the reaction the catalyst was separated from the reaction mixture using warm water (the catalyst was soluble in warm water and separated from the reaction products). The solid residue was purified by washing with ethanol and crystallized from hot ethanol to give the desired product. The water of the aqueous filtrate containing [mim]C_6F_5O evaporated and C_6F_5O was dried under reduced pressure to give the pure recycled catalyst which was weighed and reused for the next run. The recycled catalyst was reused five times to catalyze the reaction without sensible decreases in the product yield (Fig. 10).

Efficiency and applicability of [mim]C_6F_5O for the synthesis of chromene derivatives were compared with those of other reported catalysts. As shown in Table 5, [mim]C_6F_5O is better than previously reported catalysts in yields and reaction times for the condensation of 4-hydroxycoumarin, benzaldehyde and malononitrile (Table 5).

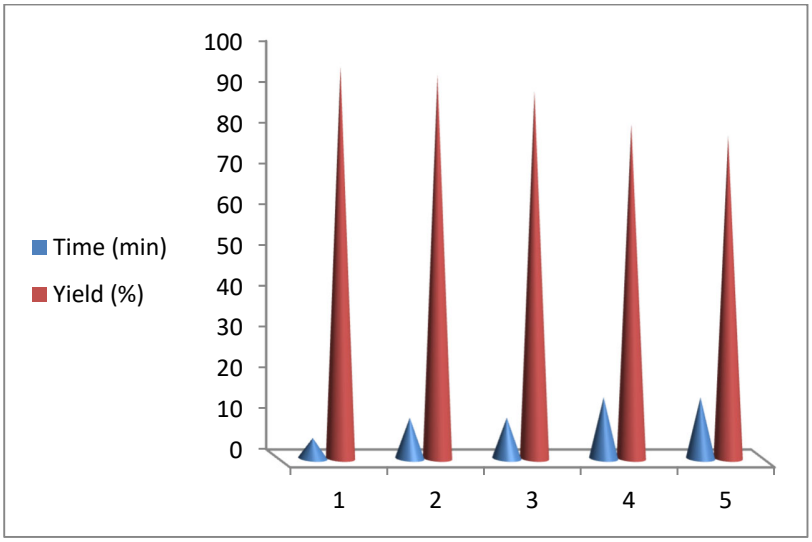


Fig. 10. Condensation of 4-hydroxycoumarin, benzaldehyde and malononitrile using recycled [mim]C_6F_5O.

In Scheme 3, a proposed mechanism for the reaction is shown. First, malononitrile reacts with aldehyde which is activated by [mim]C_6F_5O to generate cyanoolefin **I** as intermediate. Then, 4-hydroxycoumarin attacks the intermediate **I** as a Michael acceptor to give **II**. Finally, cyclocondensation of **II** creates intermediate **III** which is converted to the desired product.

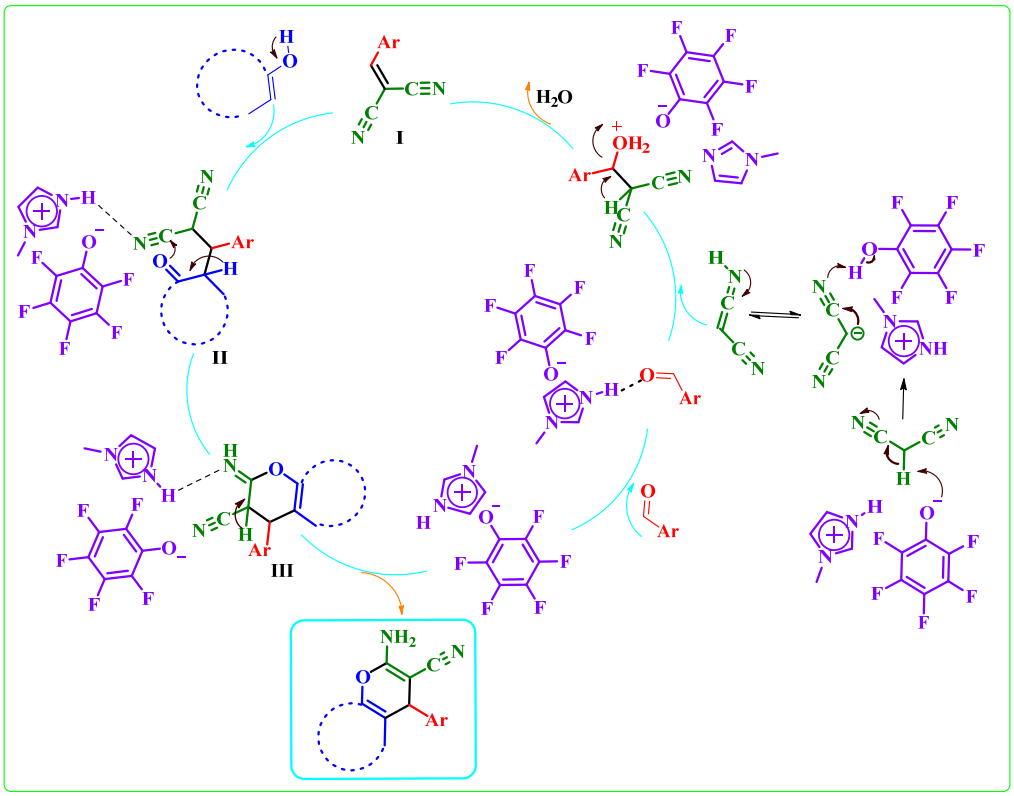
4. Conclusions

In conclusion, we have designed to synthesize [mim]C_6F_5O as the first nano ionic liquid with perfluorinated anionic tag t to generate a reusable and task-specific catalyst for the synthesis of chromemes. Efficiency, high yields, short reaction times, clean reaction profile, solvent-free condition, simplicity of preparation and recyclability of catalyst are some advantages of the described protocol. We think that this study can open up a new and promising insight into the course of rational design, synthesis and applications of task-specific nano ionic liquid with perfluorinated anionic tags for various purposes. Since that development of nano ionic liquid with perfluorinated anionic tags is more demanded for the fluorous biphasic catalysis [1b], further systematic research on knowledge-based development of this research field is going on in our research group.

Table 5. Comparison of the results in the synthesis of chromene derivatives with different catalysts.

Entry	Reaction condition	Catalyst loading	Time (min)	Yield[a] (%)	Ref.
1	[mim]C_6F_5O, solvent- free, 100 °C	10 mol %	5	96	-[a]
2	Starch solution, 50 °C	4 ml	25	95	[21]
3	SBPPSP, H_2O/EtOH, Reflux	0.06 g	12	92	[23]
4	aq. K_2CO_3, MW (540W)	10 ml saturated solution	3.2	90	[25]
5	AVOPc-MNPs, solvent- free, r.t	0.02 g	20	92	[26]
6	TiO_2 Nanowires, H_2O/EtOH, Reflux	0.03 mmol	60	90	[22]
7	DBU, H_2O, Reflux	10 mol %	7	92	[33]
8	TBAB, H_2O, Reflux	10 mol %	45	91	[34]
9	Nano ZnO, H_2O, 70 °C	10 mol %	180	87	[35]
10	magnetic nano-organocatalyst, H_2O, Reflux	1.5 mol %	10	78	[36]
11	[DMAP-PEG1000-DIL][BF_4], H_2O, Reflux	0.1 mmol	30	92	[37]
12	CTMAB-bentonite, H_2O/EtOH, 70 °C	0.03 g	6	89	[38]
13	$H_6[P_2W_{18}O_{62}]$. $18H_2O$, H_2O/EtOH, Reflux	1 mol %	30	89	[39]

[a]This work.



Scheme 3. Proposed mechanism for the synthesis of chromenes promoted by [mim]C_6F_5O.

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