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## Introduction

Reduction of aromatic nitro compounds to the corresponding amines is of immense industrial importance as they are widely used as intermediates for dyes, pharmaceuticals and agrochemicals.<sup>1</sup> Although a number of reducing reagents are available in the literature for reduction of different functional groups, the development of mild, neutral, and selective reducing systems still attracts a great deal of attention to organic chemists.<sup>2</sup> Sodium borohydride a well known reducing agent and it has wide applications in organic synthesis because of its ready availability, ease of handling, and low cost.3 A variety of systems have been reported for this transformation, such as catalytic hydrogenation,<sup>4</sup> metallic reagents in acidic media<sup>5</sup> and heterogeneous catalysts such as Pd-C and Pt-C.<sup>6</sup> A major problem with the aromatic nitro compound reduction is the use of expensive catalysts, high reaction times and temperatures. Transfer hydrogenation requires only mild conditions; offers enhanced selectivity and closed pressure systems involving hazardous hydrogen can be avoided.<sup>7</sup>

Recently much attention is being given to green chemistry which is a chemical methodology to decrease or eliminate the use or generation of hazardous substances in the design, preparation and application of chemical production.<sup>8</sup> It is well known that ionic liquids are recognized as an excellent reaction media and catalysts with considerable potential, which have been successfully exploited as alternatives to molecular solvents in transition metal-catalyzed reactions, such as hydrogenation, hydroformylation, Heck reaction, epoxidation and biomass conversion.<sup>9</sup>

# Transition metal based ionic liquid (bulk and nanofiber composites) used as catalyst for reduction of aromatic nitro compounds under mild conditions

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lonic liquid (1,1'-hexane-1,6-diylbis (3-methylpyridinium) tetrachloronickelate (II)) and PVDF-IL  $([C_6(mpy)_2][NiCl_4]^{2-})$  nanofiber composites are synthesized and used as catalysts for the reduction of nitroarenes with NaBH<sub>4</sub>/H<sub>2</sub>O system at ambient temperature. Ionic liquid containing nickel halide anion well dispersed on the PVDF nanofibers. It efficiently catalyzes the reduction of functionalized nitroarenes to the corresponding substituted anilines, avoiding the need for inert atmosphere, and additional base or other additives. The catalytic system gives good yields with other functional groups remaining intact.

NO<sub>2</sub>

Х

In continuation of our progressive investigation into the application of green methodology, we are strongly interested in the development of reduction of nitro groups using a cheap reagent with easy operation in water without any organic solvent, a methodology which would have some advantages in terms of cost, safety, simple operation, human health and environmental concerns as compared with use of an organic solvent. Recently ionic liquids containing transition metal complexes have been studied for their magnetic behavior.<sup>10</sup> We have earlier reported the synthesis and characterization of pyridinium based dicationic ionic liquids with anions containing transition metal complexes. They have been tested as catalysts for hydrogen generation and showed excellent catalytic activity.11 Therefore, here we wish to report the same ionic liquid tetrachloronickelate (II) anion with dicationic counter ions for the reduction of aromatic nitro compounds with NaBH<sub>4</sub> in water without any organic solvent. To the best of our knowledge, this is the sole example of an ionic liquid with anion containing transition metal complexes being used in such a capacity (Scheme 1). The structure of tetrachlor-



NaBH₄

 $[C_6(mpy)_2][NiCl_4]^2$ 

X

 $NH_2$ 

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Scheme 2 Tetrachloronickelate (II) anion with pyridinium dicationic counter ions ( $[C_6(mpy)_2][NiCI_4]^{2-}$ ).

onickelate (II) anion with dicationic counter ions is shown in Scheme 2.

The ionic liquid 1,1'-hexane-1,6-diylbis (3-methylpyridinium) tetrachloronickelate (II) ( $[C_6(mpy)_2][NiCl_4]^{2-}$ ) act as reaction media as well as catalyst. At room temperature and without a catalyst, only a negligible amount of hydrogen is released in aqueous solution of NaBH<sub>4</sub>. By adding a suitable catalyst, the hydrogen generation rate is significantly enhanced. The hydrolysis reaction is exothermic and proceeds according to the following equation.

$$NaBH_4 + 2H_2O \xrightarrow{Catalyst} NaBO_2 + 4H_2\uparrow$$
 (1)

It is well known that the ionic liquid  $[C_6(mpy)_2][NiCl_4]^{2^-}$  is composed of organic cation and inorganic anion. The advantages of nickel halide anion can play as catalyst and has vital role in this reduction reaction. In acidic medium the hydrolysis of NaBH<sub>4</sub> is initiated by the attack of hydronium ion on the borohydride anion. The reduction in the ionic liquid/ water system starts from the migration of BH<sub>4</sub><sup>-</sup> from the water phase by the onium cation of the ionic liquid dissolved in water.

### **Results and discussion**

Initially, we studied the reduction of nitrobenzene catalyzed by tetrachloronickelate (II) anion with dicationic counter ions using different solvents in order to assess the best reaction conditions (Table 1). In the optimization phase, it was observed that with use of MeOH, the reaction was completed in 5 h and the yield was much lower than water. The complete conversion was not observed in THF and lots of by-products

Table 1 Nitrobenzene reduction with different solvents <sup>a</sup>					
Entry	Solvent	Time (h)	Yield <sup>b</sup>		
1	$H_2O$	0.15	90		
2	MeOH	5	62		
3	THF	24	<30		
4	EtOAc	24	$0^{c}$		

<sup>*a*</sup> Reaction conditions: Substrate (1 mol), NaBH<sub>4</sub> (8 mol),  $[C_6(mpy)_2][NiCl_4]^{2-}$  (0.05 mol), rt. <sup>*b*</sup> Isolated yield. <sup>*c*</sup> Reaction not completed.

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Table 2	2	Effect	of	NaBH₄	on	nitrobenzene	reduction
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Entry	NaBH <sub>4</sub> (mol)	Time (min)	Yield $(\%)^b$
1	4	15	80
2	6	15	83
3	8	15	90

<sup>*a*</sup> Reaction conditions: Substrate (1 mol),  $[C_6(mpy)_2][NiCl_4]^{2-}$  (0.05 mol), H<sub>2</sub>O (10 mL), rt. <sup>*b*</sup> Isolated yield.

were obtained. In the case of EtOAc, the aniline was obtained in trace amounts after a few hours, there is no significant change observed even after 24 h. The spectral data has shown the side products and no formation of aniline (Table 1, entries 1–4). These results show that, as expected, the nitro group is more easily reduced in water as compared with other solvents. We found that water was the best solvent for this reaction.

The reduction of nitrobenzene was chosen as a model reaction to test the catalytic activity of the ionic liquid  $[C_6(mpy)_2]$ [NiCl<sub>4</sub>]<sup>2-</sup>. This reaction was carried out in water at room temperature (rt). Nitrobenzene was efficiently reduced in 15 min and gave excellent yields. The effect of the amount of NaBH<sub>4</sub> on the reduction reaction was investigated using 0.05 mol of the catalyst [C<sub>6</sub>(mpy)<sub>2</sub>][NiCl<sub>4</sub>]<sup>2-</sup> and 1 mol nitrobenzene. The results showed that by increasing the amount of NaBH<sub>4</sub>, the percentage of yield increased. The results are presented in Table 2. 8 mol was the best and gave a high yield. In a similar manner the variation of catalytic activity was also studied. The nitrobenzene reduction was successfully reduced using a very small amount of catalyst (0.01 mol). The reaction completed in 45 min and gave 85% yield. By increasing the amount of catalyst, there is a change in reaction time and yield. 0.05 mol was the best and gave very good yield (Table 3). For all other nitro compounds reactions reported hereafter, the catalyst (0.05 mol) and NaBH4 (8 mol) was used unless otherwise stated.

The results presented in Table 4 indicate the generality of the method and efficacy of these new catalytic systems. The reduction of 2-substituted nitrophenol using IL with tetrachloronickelate (II) anion gives lower yields than the reduction of 4-substituted nitrophenol (Table 4, entries 2 and 3). In the reduction of the nitro compounds no demethylation was observed and gave 76 and 85% yield without affecting the C– CH<sub>3</sub> bond. In the case of 4-nitroaniline the reaction was completed in 15 min (Table 4, entry 6).

Table 3 Effect of catalyst $[C_6(mpy)_2][NiCl_4]^{2-}$ on nitrobenzene reduction <sup>a</sup>						
Entry	Catalyst (mol)	Time (min)	Yield $(\%)^b$			
1	0.01	45	85			
2	0.03	30	90			
3	0.05	15	90			

 $^a$  Reaction conditions: Substrate (1 mol), NaBH<sub>4</sub> (8 mol), H<sub>2</sub>O (10 mL), rt.  $^b$  Isolated yield.

Table 4 Aromatic reduction of various nitroarenes<sup>a</sup>

Entry	Substrate	Product	Time	Yield (%) <sup>b</sup>
1	Nitrobenzene	Aniline	15 min	90
2	2-Nitrophenol	2-Aminophenol	15 min	80
3	4-Nitrophenol	4-Aminophenol	5 min	85
4	3-Nitrotoulene	3-Toluidine	15 min	76
5	4-Nitrotoulene	4-Toludine	30 min	85
6	4-Nitroaniline	1,4-Phenylenedine	15 min	80
7	Nitrobenzene	Aniline	24 h	$0^c$
8	4-Chloro nitrobenzene	4-Chloro aniline	4 h	55
9	3-Chloro nitrobenzene	3-Chloro aniline	4 h	88
10	4-Bromo nitrobenzene	4-Bromo aniline	4 h	80
11	3-Iodo nitrobenzene	3-Iodo aniline	4 h	65

<sup>*a*</sup> All reactions were carried out with Molar ratio: 1 : 8 : 0.05,

Substrate/NaBH<sub>4</sub>/IL, H<sub>2</sub>O (10 mL). <sup>b</sup> Isolated yield. <sup>c</sup> Without catalyst (NaBH<sub>4</sub> only).

The halogenated nitroarenes were reduced to the corresponding anilines without any dehalogenation and the products were isolated with 55–88% yield (Table 4, entries 8– 11). In the case of the reduction with sodium borohydride itself without the catalyst, no reaction preceded (Table 4, entry 7). The catalyst was highly active for the reduction of nitro and other functional groups such as halogen, OH, NH<sub>2</sub>, CH<sub>3</sub> were not affected. All these compounds were reduced in excellent yields affording a single product, which reduced the difficulties of separation of the products from unreacted substrates.

Recently ionic liquid based nanofibers have gained much attention.<sup>12</sup> Electrospinning produces fibers in submicrometer sizes by applying electric force to polymer solutions or melts. The electric force extrudes polymer jets from a spinneret and stretches them from millimeter to submicrometer diameters through a whipping-like motion. Due to the success of our IL based transition metal complexes in nitro compounds reduction, we extended our work to synthesize nanosized materials and apply them to the aromatic nitro compounds reduction reaction. Since this transformation requires catalysts with high surface area and high acidic active sites, it seems that nanosized materials which possess such characteristics could be suitable for this purpose. Nanostructured catalysts, such as polymer-supported amorphous Ni-B nanoparticles<sup>13</sup> silica supported gold nanoparticles,<sup>14</sup> and Faujasite NaY zeolite<sup>15</sup>, have been employed in the catalytic transfer hydrogenation of nitroarenes. However, these reactions are usually conducted under refluxing conditions, a process that requires several hours of time. Furthermore, the activity of most of these catalysts decreases with subsequent recycling. In this work, electrospinning of ionic liquid containing transition metal complexes blended with polyvinylidene fluoride (PVDF) solution was demonstrated. PVDF- $[C_6(mpy)_2][NiCl_4]^{2-}$  nanofiber composites were tested in the aromatic nitro compounds reduction. The performance of the catalyst was excellent. The reaction was carried out in mild reaction conditions. Separation of the catalyst from the reaction mixture was simple and there was no deactivation of catalyst in subsequent recycling. The performance of the nanofiber composite

catalyst was more effective than the bulk catalyst  $([C_6(mpy)_2][NiCl_4]^{2^-}).$ 

Fig. 1 shows the SEM images of PVDF nanofiber and PVDF- $[C_6(mpy)_2][NiCl_4]^{2-}$  composite nanofibers with different  $[C_6(mpy)_2]$ [NiCl<sub>4</sub>]<sup>2-</sup> content. As can be seen from Fig. 1a, the PVDF nanofibers have a diameter ranging from 150-200 nm. The morphology of electrospun PVDF- $[C_6(mpy)_2]$ [NiCl<sub>4</sub>]<sup>2</sup> composite nanofibers produced from PVDF-[C<sub>6</sub>(mpy)<sub>2</sub>][NiCl<sub>4</sub>]<sup>2-</sup> solution with 2.5% and 5%  $[C_6(mpy)_2][NiCl_4]^{2-}$  content (Fig. 1b and 1c) increased dramatically from 470 nm to 575 nm. TEM of the resulting electrospun fibrous mat in Fig. 1d, a uniform distribution of [C<sub>6</sub>(mpy)<sub>2</sub>][NiCl<sub>4</sub>]<sup>2</sup> catalyst on the surface of the PVDF nanofibers can be seen. Fig. 2 is the energy dispersive X-ray spectrum of PVDF-[C<sub>6</sub>(mpy)<sub>2</sub>][NiCl<sub>4</sub>]<sup>2-</sup> nanofiber composites. Fig. 2a depicts the elements of C and F only for pure PVDF nanofibers where as Fig. 2b and 2c indicates Ni and Cl which isn't present in Fig. 2a. It reveals that the ionic liquid containing transition metal anion successfully incorporated on PVDF nanofiber through electrospinning.

Fig. 3 shows the IR spectra obtained for PVDF and PVDF-IL nanofiber composites. The major absorption bands at1403, 1181, 870 and 854 cm<sup>-1</sup> correspond to the C-H and C-F groups for the pure PVDF, which are in good agreement with PVDF-IL nanofiber composites. The pure IL was also tested and the characteristic peaks are 3046, 730, 683, 2939, 1500 cm<sup>-1</sup>. The characteristic peaks of the IL can be identified from the electrospun fibers and the specific peak value of each peak can be observed on the IL spectra.

Addition of ionic liquid was expected to increase the conductivity and consequently further improve the spinning performance. As expected, electrospinning of PVDF became smoother with the presence of ionic liquid  $[C_6(mpy)_2][NiCl_4]^{2^-}$ . During electrospinning, a smooth and steady polymer jet was observed with no spinneret blockage. Thick and detachable fiber mats were obtained within hours.

The reduction of several substrates was also investigated over a nanosized material PVDF- $[C_6(mpy)_2][NiCl_4]^{2-}$  catalyst under the optimized condition. The reduction of nitrobenzene was chosen as a model reaction to optimize the reaction conditions (Table 5). In a typical reaction, nitrobenzene (1 mol), different loadings of PVDF-[C<sub>6</sub>(mpy)<sub>2</sub>][NiCl<sub>4</sub>]<sup>2-</sup> nanofiber composite 2.5 wt% and 5 wt% respectively and 10 mL of water were stirred at rt for a few seconds. Then NaBH<sub>4</sub> (8 mol) was added within 3 min. 2.5 wt% of PVDF-[C<sub>6</sub>(mpy)<sub>2</sub>][NiCl<sub>4</sub>]<sup>2-</sup> nanofiber composite (0.1 g) was used as a catalyst, a trace amount of aniline was observed in thin layer chromatography (TLC) after 24 h but NMR spectra has not shown any peak for amine group. In the case of 5 wt% (0.1 g) reaction was not completed, but here also trace amount of aniline was observed. It shows that with lower loadings or lower mass of the catalyst there were not sufficient catalytic sites available for the reduction reaction. Ni content present in the ionic liquid  $[C_6(mpy)_2][NiCl_4]^{2-}$  plays a vital role in the reduction reaction. It is dependent on the concentration of IL  $[C_6(mpy)_2][NiCl_4]^{2-1}$ used to immobilize in the PVDF. Its noteworthy to mention



**Fig. 1** SEM images of electrospun PVDF nanofibers (a) and PVDF- $[C_6(mpy)_2][NiCl_4]^2^-$  composite nanofibers with different  $[C_6(mpy)_2][NiCl_4]^{2^-}$  content: (b) 2.5 wt%, (c) 5 wt%. (d) TEM image of PVDF- $[C_6(mpy)_2][NiCl_4]^{2^-}$  nanofiber composite (2.5 wt%) Inset: single nanofiber image.

here that the amount of Ni content present in the compound  $[C_6(mpy)_2][NiCl_4]^{2-}$  is just 3.7 mg which is very small. So we increased the catalyst (5 wt% of PVDF- $[C_6(mpy)_2][NiCl_4]^{2-}$  nanofiber composite) amount to 0.3 g, as expected the conversion of nitrobenzene and product yield increased, which is due to the proportional increase in the number of active sites. However, no further improvement was observed with higher loads. The optimal catalyst load showed to be 5 wt% of PVDF- $[C_6(mpy)_2][NiCl_4]^{2-}$  nanofiber composite (0.3 g) which produced aniline as the only product of the reaction in

90% yield after 10 min (Table 6, entry 1). As can be seen in Table 6, electron withdrawing/donating groups do not have a significant influence on the reaction times and yields. In all cases, amines were found to be the only product of the reactions. The present method was highly efficient for the aromatic nitro compound reduction. The results in Table 4 (entries 1–6, 8) and Table 6 (entries 1–6) clearly indicate that the PVDF-[C<sub>6</sub>(mpy)<sub>2</sub>][NiCl<sub>4</sub>]<sup>2-</sup> nanofiber composite is more active than the bulk catalyst [C<sub>6</sub>(mpy)<sub>2</sub>][NiCl<sub>4</sub>]<sup>2-</sup>.



Fig. 2 EDX images of nanofiber composites: (a) Pure PVDF, (b) PVDF-[ $C_6(mpy)_2$ ][NiCl<sub>4</sub>]<sup>2-</sup> (2.5 wt%), (c) PVDF-[ $C_6(mpy)_2$ ][NiCl<sub>4</sub>]<sup>2-</sup> (5 wt%).



Fig. 3 FTIR spectra of PVDF- $[C_6(mpy)_2][NiCl4]^{2-}$  nanofiber composites.

The reductions of nitro compounds using nanocrystalline magnesium oxide-stabilized palladium (0) have been studied,<sup>6d</sup> where the reduction of nitrobenzene to aniline took place for 2 h using THF as a solvent at room temperature (under H<sub>2</sub> atmosphere) and 4-nitro phenol to 4-amino phenol reaction was completed in 1 h. But it is surprisingly noted that these reductions were completed in 10 min and 5 min respectively using PVDF- $[C_6(mpy)_2][NiCl_4]^{2-}$  nanofiber composite. Both the catalyst bulk as well as nanofiber composite is more effective than several other catalytic systems reported in the literature such as Ni-stabilized zirconia,16 Nickel based oxide catalysts,<sup>17</sup> Ni nanoparticles-polyvinylamine/SBA-15,<sup>18</sup> Perovskite-type LaFeO3 nanoparticles.<sup>1f</sup> Furthermore most of these systems require longer reaction times under refluxing conditions or microwave irritation. The results of this work show that the present process is more efficient than previous works as evident from the shorter reaction times. It is a new, simple and effective method in comparison with an expensive catalyst.

The recycling of catalyst was examined. 4-nitrophenol was studied to demonstrate the recyclability and stability of the catalyst; it was separated from the reaction mixture, dried at 80  $^{\circ}$ C for 5–8 h. The recovered catalyst was reused in the next run under the same conditions (Table 6, entry 3). The results in Table 7 indicate that there is no appreciable difference in the

Table 5 Optimization of reaction conditions for nitrobenzene reduction using PVDF-[ $C_6(mpy)_2$ ][NiCl\_4]<sup>2-</sup> nanofiber composite<sup>a</sup>

Entry	X (wt%)	Catalyst amount (g)	Solvent	Time	Yield <sup>b</sup>
1 2	2.5 5	0.1 0.1	$H_2O$ $H_2O$	24 h 24 h	0 <i>c</i>
3	5	0.3	$H_2O$	10 min	90

<sup>*a*</sup> Substrate (1 mol), NaBH<sub>4</sub> (8 mol), PVDF- $[C_6(mpy)_2][NiCl_4]^{2-}$ nanofiber composite with different  $[C_6(mpy)_2][NiCl_4]^{2-}$  content (X wt%), rt. H<sub>2</sub>O (10 mL). <sup>*b*</sup> Isolated yield. <sup>*c*</sup> Reaction not completed.

**Table 6** Reduction of nitro compounds by PVDF- $[C_6(mpy)_2][NiCl_4]^{2-}$  nanofiber composite in NaBH<sub>4</sub>/H<sub>2</sub>O system<sup>a</sup>



Entry	Substrate	Product	Time (min)	Yield (%) <sup>b</sup>
1	Nitrobenzene	Aniline	10	90
2	2-Nitrophenol	2-Aminophenol	3	80
3	4-Nitrophenol	4-Aminophenol	5	90
4	3-Nitrotoulene	3-Toluidine	10	85
5	4-Nitrotoulene	4-Toludine	6	85
6	4-Chloro nitrobenzene	4-Chloro aniline	15	55

 $^a$  All reactions were carried out with Molar ratio: 1 : 8 Substrate/ NaBH<sub>4</sub>, PVDF-[C<sub>6</sub>(mpy)<sub>2</sub>][NiCl<sub>4</sub>]<sup>2-</sup> nanofiber composite (0.3 g, H<sub>2</sub>O (10 mL), rt.  $^b$  Isolated yield.

yields after four runs. The recovered PVDF- $[C_6(mpy)_2][NiCl_4]^{2^-}$  nanofiber composite after the fourth run was characterized by SEM, EDX and FT-IR. As shown in Fig. 4, SEM and EDX of the recycled PVDF- $[C_6(mpy)_2][NiCl_4]^{2^-}$  nanofiber composite catalyst did not show significant change in comparison with the fresh catalyst (Fig. 1 and 2). As depicted in Fig. 5 all characteristic peaks can be obviously observed from the recycled nanofiber composite. This observation confirms that the PVDF- $[C_6(mpy)_2][NiCl_4]^{2^-}$  nanofiber composite is stable under the reaction conditions and is not affected by the reactants. The extra peak at 1500 cm<sup>-1</sup> and 1020 cm<sup>-1</sup> (recycled) may be due to unreacted starting materials.

### Conclusion

In conclusion, the reduction of nitroarenes to their corresponding aniline was studied using bulk catalyst ionic liquid with anions containing nickel halide and PVDF- $[C_6(mpy)_2][NiCl_4]^{2-}$  nanofiber composite. It proceeds under mild conditions without affecting various functional groups on the aromatic ring. The reaction was performed at room temperature. It's noteworthy to mention here that a very small amount of Ni content present in the dicationic IL was sufficient for the reduction processes of nitroarenes. PVDF-

<b>Table 7</b> Reusability of the nanofiber composite $PVDF-[C_6(mpy)_2][NiCl_4]^{2-}$	
catalyst for 4-nitrophenol <sup>a</sup>	

Run	1	2	3	4
Гime (min)	5	5	5	5
<i>ield<sup>b</sup></i>	90	90	90	88

<sup>*a*</sup> Reaction conditions: Similar to Table 6, entry 3. <sup>*b*</sup> Isolated yield.



Fig. 4 SEM and EDX images of PVDF-[C<sub>6</sub>(mpy)<sub>2</sub>][NiCl<sub>4</sub>]<sup>2-</sup> nanofiber composites (5 wt%): (a) before reaction, (b) and (c) after 4th recycle, Inset: photo image.

 $[C_6(mpy)_2][NiCl_4]^{2^-}$  nanofiber composite is more active than the bulk  $[C_6(mpy)_2][NiCl_4]^{2^-}$  catalyst. PVDF- $[C_6(mpy)_2][NiCl_4]^{2^-}$  nanofiber composites having high specific surface area were readily prepared by electrospinning. It is exhibited very good activity and yields. The advantages of this method: ready availability and ease of operation, rapid reduction, good yields of substituted amines, avoidance of strong acid media, no equipment of pressure apparatus and lower cost. PVDF- $[C_6(mpy)_2][NiCl_4]^{2^-}$  nanofiber composite was found to be superior to its IL nanocomposite analogue. The report overcomes the challenges in this field in terms of reaction conditions and recovery of catalyst and product.

## **Experimental section**

#### General information

All nitro compounds were purchased from Sigma Aldrich. The reaction products are commercially available compounds and



Fig. 5 FT-IR spectra of PVDF-[C<sub>6</sub>(mpy)<sub>2</sub>][NiCl<sub>4</sub>]<sup>2-</sup> nanofiber composites (5 wt%) after recycling.

their analytical data were in perfect agreement with the authentic samples.

# $\label{eq:2.1} \begin{array}{l} \mbox{Preparation of 1,1'-hexane-1,6-diylbis (3-methylpyridinium)} \\ \mbox{tetrachloronickelate (II) ([C_6(mpy)_2] [NiCl_4]^{2-})} \end{array}$

The ionic liquid was synthesized (Scheme 2) and discussed in detail in our previous reported work.<sup>11</sup> 3-Methyl pyridine (0.04 mol, 3.89 mL) is dissolved in 25 mL toluene at RT. 1, 6-dibromohexane (0.02 mol, 3.07 mL) was added slowly into the flask within 30 min in an ice bath. The stirring was continued at this temperature for 30 min before elevating the temperature to 110 °C for 12 h. An off-white solid was formed. Upon completed the reaction, the solvent was removed by decanting. The reaction mixture was extracted with ethyl acetate (3 × 30 mL) and then dried under vacuum oven at 70 °C for 5 h.

1,1'-hexane-1,6-diylbis (3-methylpyridinium) dibromide  $[C_6(mpy)_2] Br_2^{-1}$ : <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>,  $\delta$  (ppm) relative to TMS) 9.09 (s, 2H), 8.98 (d, 2H, *J* = 8 Hz), 8.43 (d, 2H, *J* = 8 Hz), 8.01 (dd, 2H, *J* = 6 Hz), 4.57 (t, 4H, *J* = 7.9 Hz), 3.49 (s, 6H), 1.91 (m, 4H), 1.30 (m, 4H). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta_H$  (ppm) 146.20, 144.76, 142.44, 139.08, 127.71, 60.55, 30.66, 25.04, 18.29.

1,1'-hexane-1,6-diylbis (3-methylpyridinium) dibromide  $[C_6(Mpy)_2] Br_2^-$  (0.007 mol) and NiCl<sub>2</sub>·6H<sub>2</sub>O (0.017 mol) were dissolved in ethanol and stirred at room temperature for four days. After completion of the reaction the solvent evaporated in rotatory evaporator to give the green color solid. The obtained product was washed with Ethyl acetate several times and dried in vacuum at 80 °C for 5 h. LRMS (FAB+) calcd for  $C_{18}H_{26}N_2Cl_4Ni\cdot(M-[NiCl_4])^+$  135.10 found 135.14

#### Electrospinning

Polymer solution of PVDF- $[C_6(mpy)_2]$ [NiCl<sub>4</sub>]<sup>2-</sup> for electrospinning were prepared by dissolving the polymer in N,N-Dimethylformamide (DMF) and stirred at 30-40 °C till to get homogeneous solution. PVDF concentration was kept at 15 wt% with respect to DMF and dicationic counter ions with tetrachloronickelate (II) anion (IL) was 2.5 and 5 wt% with respect solvent. The electrospinning apparatus used in this study consisted of a high voltage power supply, syringe pump, syringe needle (0.21 mm.), and grounded collector (aluminum foil). The needle was connected to the high voltage supply. The spinning distance between the tip of needle and the collector was in the range of 18-21 cm. Positive voltage of 20-22 KV was applied to polymer solutions. The solution flow rates were controlled with syringe pump ranging from 2–3 mL  $h^{-1}$ . All electrospinning experiments were carried out at room temperature.

#### General procedure for aromatic nitro compounds reduction

To a solution of nitro compounds and IL (tetrachloronickelate (II) anion with dicationic counter ions) in water was stirred at room temperature for a few seconds. Then weighed amount of NaBH<sub>4</sub> added in portion by slowly within 3 min. The progress of the reaction was monitored by Thin Layer Chromatography (TLC) using hexane/EtOAc (7 : 3) as an eluent. After completion of the reaction, the reaction mixture was quenched with NaCl solution and the product was extracted from the aqueous

medium by EtOAc (4  $\times$  50 mL) as an organic layer. Then, the combined organic solutions were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and solvent evaporated by rotary evaporator, so, a pure product was obtained. The resulting products were analyzed by <sup>1</sup>H NMR and IR spectroscopic methods.

**Spectral data of aniline derivatives.** All compounds were identified by spectral comparison with samples purchased from commercial sources.

#### Table 4, entries 1-6, 8-11

Aniline. IR (neat)  $\nu$  3446, 3356, 3212, 3070, 3034, 1619, 1600, 1497, 1466, 1289, 1174, 879, 750, 690 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.60 (bs, 2H), 6.69 (d, 2H), 6.78 (t, 1H), 7.18 (d, 2H)

**2-Aminophenol.** IR (KBr)  $\nu$  3373, 3302, 3052, 2848, 2583, 2031, 1761, 1599, 1510, 1459, 1279, 1084, 891, 845, 739 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  4.40 (bs, 2H), 6.32 (ddd, 1H), 6.36 (ddd, 1H), 6.50 (ddd, 1H), 6.59 (ddd, 1H).

**4-Aminophenol.** IR (KBr)  $\nu$  3348, 3280, 1864, 1613, 1508, 1471, 1384, 1091, 966, 822, 748, 646 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  4.32 (bs, 2H), 6.39 (d, 2H), 6.46 (d, 2H), 8.30 (s, 1H)

**3-Toluidine.** IR (neat)  $\nu$  3446, 3358, 3033, 2919, 1620, 1492, 1376, 1291, 1169, 995, 853, 772, 689 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.11 (s, 3H), 4.86 (bs, 2H), 6.27 (ddd, 1H), 6.34 (dd, 1H), 6.35 (ddd, 1H), 6.87 (dd, 1H)

**4-Toluidine.** IR (neat)  $\nu$  3417, 3337, 3220, 3094, 3010, 2912, 2859, 2357, 1878, 1621, 1580, 1513, 1323, 1280, 1268, 1177, 1122, 1071, 952, 874, 830, 811, 757, 672 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  2.23 (s, 3H), 3.50 (bs, 2H), 6.57 (d, 2H), 6.96 (d, 2H)

**1, 4-Phenylenedine.** IR (KBr) v 3409, 3383, 3372, 3200, 3044, 3008, 2895, 1867, 1629, 1604, 1513, 1374, 1309, 1260, 1127, 1064, 1040, 972, 822, 795, 665 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  4.13 (bs, 4H), 6.31 (s, 4H).

**4-Chloroaniline.** IR (KBr)  $\nu$  3472, 3382, 3198, 1881, 1614, 1492, 1288, 1181, 1089, 1005, 819, 637 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.63 (bs, 2H), 6.60 (d, 2H), 7.10 (d, 2H).

**3-Chloroaniline.** IR (neat)  $\nu$  3367, 3214, 3032, 1619, 1596, 1484, 1300, 1266, 1162, 1076, 992, 887, 848, 766, 680 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.70 (bs, 2H), 6.53 (ddd, 1H), 6.66 (dd, 1H), 6.72 (ddd, 1H), 7.06 (dd, 1H)

**4-Bromoaniline.** IR (KBr)  $\nu$  3446, 3348, 3033, 1869, 1600, 1488, 1298, 1173, 1128, 1069, 816 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.64 (bs, 2H), 6.56 (d, 2H), 7.23 (d, 2H)

**3-Iodoaniline.** IR (neat) v 3445, 3357, 3211, 3069, 3012, 1922, 1617, 1599, 1566, 1519, 1476, 1439, 1268, 1153, 1059, 851, 681, 657 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.63 (bs, 2H), 6.58 (ddd, 1H), 6.67 (dd, 1H), 6.87 (ddd, 1H), 7.08 (dd, 1H)

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