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Synthesis, Characterisation, and Determination of Physical Properties of New Two-Protonic Acid Ionic Liquid and its Catalytic Application in the Esterification

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A new ionic liquid was synthesised, and its chemical structure was elucidated by FT-IR, 1D NMR, 2D NMR, and mass analyses. Some physical properties, thermal behaviour, and thermal stability of this ionic liquid were investigated. The formation of a two-protonic acid salt namely 4,4'-trimethylene-N,N'-dipiperidinium sulfate instead of 4,4'-trimethylene-N,N'-dipiperidinium hydrogensulfate was evidenced by NMR analyses. The catalytic activity of this ionic liquid was demonstrated in the esterification reaction of *n*-butanol and glacial acetic acid under different conditions. The desired acetate was obtained in 62–88 % yield without using a Dean–Stark apparatus under optimal conditions of 10 mol-% of the ionic liquid, an alcohol to glacial acetic acid mole ratio of 1.3 : 1.0, a temperature of 75–100°C, and a reaction time of 4 h. α -Tocopherol (α -TCP), a highly efficient form of vitamin E, was also treated with glacial acetic acid in the presence of the ionic liquid, and *O*-acetyl- α -tocopherol (Ac-TCP) was obtained in 88.4 % yield. The separation of esters was conducted during workup without the utilisation of high-cost column chromatography. The residue and ionic liquid were used in subsequent runs after the extraction of desired products. The ionic liquid exhibited high catalytic activity even after five runs with no significant change in its chemical structure and catalytic efficiency.

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Introduction

Catalysis is a vital topic in organic chemistry, and has been employed in a broad range of sectors, products, and processes. The current trend in catalysis research is to design greener catalysts and eco-friendly technologies, as well as directing the activities towards sustainability and investigating the catalytic activity under realistic conditions regarding temperature and pressure.

Natural and synthetic esters have been utilised in different fields, including pharmaceuticals, perfumes, flavours, cosmetics, adhesives, detergents, solvents, plasticisers, lubricants, electronic materials, and daily and fine chemicals, etc.^[1,2] Low molecular mass esters have been widely found in fragrances and essential oils^[3] and pheromones.^[4]

The carboxylic acid esters can be synthesised using various chemical reactants, catalysts, and reaction media.^[5] Although numerous papers have appeared for the esterification reaction, the development of an efficient synthesis of carboxylic acid esters using carboxylic acids instead of acid anhydride is still an exciting research topic.

The Fischer esterification is the conventional and most common process for the esterification reaction.^[6] The catalytic

esterification has been reported using various catalysts;^[7–16] nonetheless, there are some drawbacks, for example

- a) use of excessive reagents and dehydration agents or Dean-Stark apparatus,
- b) use of expensive, toxic, or corrosive reagents and catalysts,
- c) limited substrate-scope, especially substrates bearing acid or base sensitive groups,
- d) use of an activated carboxylic acids together with a stoichiometric base,
- e) the generation of a large amount of waste during the process,
- f) use of non-recyclable catalysts and inactivation of catalytic sites, and
- g) a tedious process for the preparation of catalysts, and the separation and purification of products.^[5]

Therefore, it is required to develop an efficient and greener methodology to overcome some drawbacks and achieve a suitable balance between the economic and ecological aspects of production.

Due to the outstanding properties of ionic liquids (ILs), such as thermal and chemical stability, low vapour pressure, and recoverability, they have been extensively employed as an



[TMDPH₂][SO₄] (II)

Scheme 1. The proposed chemical structures for the new ionic liquid.

	β	i.	
H. + /2 - 3-	-4	4-	3 ⁻¹ - ² ⊕ .H
N_₀_	5΄ α	α 5 -	⁶ N
н́			н́

Table 1. The 1D NMR data of [TMDPH₂][SO₄] in DMSO- d_6 and D₂O

Atom	DMSO- d_6		D ₂ O			
	$\delta_{\rm H}[{\rm ppm}]$	<i>J</i> [Hz]	$\delta_{\rm C}$ [ppm]	$\delta_{ m H}[m ppm]$	<i>J</i> [Hz]	$\delta_{\rm C}$ [ppm]
NH ⁺ (<i>eq</i>)	8.46	br s	_	_	br s	_
$\mathrm{NH}^+(ax)$	8.17	br s			br s	
CH-2, CH-2', CH-6, and CH-6'(eq)	3.23	d, 12.1	43.57	3.29	d, 12.8	44.15
CH-2, CH-2', CH-6, and CH-6'(ax)	2.82	dd, 11.5 and 22.6	43.57	2.85	td, 2.5 and 12.9	44.15
CH-3, CH-3', CH-5, and CH-5'(eq)	1.77	d, 13.2	28.57	1.83	d, 14.0	28.37
CH-3, CH-3', CH-5, and CH-5'(ax)	1.26-1.18	М	28.57	1.27-1.17	m	28.37
CH-4 and CH-4'	1.53-1.43	М	35.64	1.53-1.46	m	34.97
CH ₂ -α	1.26-1.18	М	32.95	1.27-1.17	m	32.76
CH ₂ -β	1.26-1.18	М	22.76	1.27-1.17	m	22.29

eco-friendly solvent and/or catalyst in a variety of reactions, such as esterification.^[17–23] In continuing our previous works on 4,4'-trimethylenedipiperidine (TMDP),^[24–26] the synthesis of a new IL was designed and carried out through stirring TMDP and sulfuric acid (98 %) in CH₂Cl₂. The chemical structure of the new ionic liquid ([TMDPH₂][SO₄]) was characterised by FT-IR, 1D NMR, 2D NMR, and mass analysis. The existence of a sulfate anion, instead of hydrogen sulfate, was evidenced by detailed ¹H NMR analyses. The physical properties of the new IL have been determined and are reported herein. The catalytic activity of the new IL was studied for the direct esterification of various carboxylic acids and alcohols under obtained optimal reaction conditions.

Results and Discussion

Synthesis and the Structure Elucidation of New Ionic Liquid

TMDP was treated with one and two equivalent(s) of sulfuric acid to investigate the two possible chemical structures of the new IL that could be formed by an acid–base reaction of TMDP bearing two piperidine rings and sulfuric acid as a two-protonic acid (Scheme 1).

Dropwise addition of two equivalents of sulfuric acid (98%) into a solution of TMDP in dichloromethane in an

ice-bath and then stirring the mixture at room temperature overnight afforded a pale yellow sticky solid. The pale yellow crystals were obtained from methanol through crystallisation (mp 74–75°C) (see Supplementary Material, Fig. S1). Further studies, including FT-IR, 1D and 2D NMR, and mass spectrometry, were conducted to find the chemical structure of the new IL.

The ¹H NMR spectrum of new IL showed two pseudo-singlet peaks at 8.46 and 8.17 ppm. Regarding the magnetic anisotropy of the chair conformation of two piperidinium rings, these protons were attributed to the protons at the equatorial and axial positions of $>NH_2^+$, respectively (see Supplementary Material, Fig. S2).^[27] The presence of acidic protons on nitrogen atoms at a downfield position showed that intramolecular hydrogen bonding in the new IL was weakened.

The chemical shift and coupling constant of the equatorial and axial hydrogens (H_{eq} and H_{ax}) of the two piperidinium rings as well as protons of the three-carbon spacer are given for the new IL in DMSO- d_6 and D₂O in Table 1. The observation of a singlet and a triplet signal at 3.63 and 7.15 ppm corresponding to H₂O and HDO, respectively, demonstrated a slow rate of exchange between H₂O and HDO (see Supplementary Material, Fig. S2). As one can see in Fig. S3 (see Supplementary Material), the protons of $>NH_2^+$ disappeared in D₂O due to fast hydrogen exchange with the deuterium of D₂O.

The carbons of new IL are detected at 43.57, 35.64, 32.95, 28.57, and 22.76 ppm and 44.15, 34.97, 32.76, 28.37, 22.29 ppm in DMSO- d_6 and D₂O, respectively (see Supplementary Material, Figs S4 and S5).

The 2D COSY spectra of new IL displayed correlations between the acidic protons of $>NH_2^+$ at 8.46 and 8.17 ppm with the equatorial and axial protons of C2, C2', C6, C6' at 3.23 and 2.82 ppm, respectively (see Supplementary Material, Fig. S6).

The reaction of TMDP and sulfuric acid was also carried out in CH₂Cl₂ at a ratio of 1 : 1 at room temperature overnight, which gave a white solid. The ¹H and ¹³C NMR spectra of the TMDP and sulfuric acid at a ratio of 1 : 1 were recorded in DMSO- d_6 (see Supplementary Material, Fig. S7). One and two equivalent(s) of sulfuric acid (98 %) was then directly added to the NMR tube containing TMDP and sulphuric acid at a ratio of 1 : 1 in DMSO- d_6 , and the ¹H NMR spectra were recorded (see Supplementary Material, Fig. S8).

The single peak of water at 3.92 ppm moved to the downfield region, and a broadened multiplet and singlet signal were observed at 4.45–4.43 and 6.96 ppm, respectively (see Figs S7a, S8a, and S8b, Supplementary Material). The ¹³C NMR spectra showed negligible shifts before and after adding sulfuric acid. The ¹H NMR spectrum of sulfuric acid was also investigated, which showed a relatively sharp singlet at 7.13 ppm in DMSO- d_6 (see Supplementary Material, Fig. S9).

The ¹H NMR spectrum of new IL did not show any peaks at a region of 4.38–5.25. Moreover, no sharp or broadened peak was detected at a range of 4.0 to 8.5 ppm and above 9.5 ppm. Therefore, the existence of excess sulfuric acid or formation of an acidic anion, namely hydrogen sulfate, could be excluded.

The infrared spectrum of new IL is shown in Figure S10 (see Supplementary Material). The broadened peak at 3407 cm⁻ can be attributed to the N-H vibration mode at the >NH₂⁺ groups. Two bands at 3034, 2923, and 1321 cm⁻¹ were assigned to the symmetric, antisymmetric stretching vibrational, and wagging mode of methylene groups in the piperidinium rings, respectively. All absorption peaks at a range of 2848 to 2524 cm⁻¹ were assigned to the N-H stretching band and their shift towards this region are probably due to the strong interactions between $> NH_2^+$ and the sulfate anion through hydrogen bonding.^[28] The deformation vibration modes of >NH₂⁺ at 1616 and 1462 cm⁻¹ are characteristic of secondary amine salts.^[28] The asymmetric and symmetric SO₂ stretching vibrations appeared at 1215, 1151, and 1029 cm⁻¹, respectively. The sharp bands at 877 and 577 cm⁻¹, as well as a medium band at 487 cm^{-1} , were assigned to the S–O stretching modes and SO₂ bending, respectively.^[29]

Electrospray ionisation-mass spectrometry (ESI-MS) analyses in the negative and positive ionisation modes were conducted on the sample. Both negative and positive ion modes of analysis gave sensitive and good spectra data. The positive ionisation spectrum of the new IL recorded prominent $[M + EtOH + NH_4]^+$ and $[M + EtOH + CO_2 + NH_4]^+$ peaks (where M corresponds to TMDP) at m/z 274.2753 and 318.3014, respectively (see Supplementary Material, Fig. S11-A). Moreover, the negative ionisation spectrum of the new IL displayed a weak ion at m/z 339.2005 assigned to $[M + H + SO_4 + CH_3OH]^-$ (see Supplementary Material, Fig. S11-B).

Based on our results, structure II was demonstrated for the new IL evidencing it to be [TMDPH₂][SO₄], and indicate that

complete deprotonation of the sulfuric acid likely occurs by TMDP under our reaction conditions.

Physical Properties of [TMDPH₂][SO₄]

The bulk amount of $[TMDPH_2][SO_4]$ could be liquefied at ~110°C in an oil bath (mp 74–75°C). The ionic conduction value (σ) of new IL was 1.82 ± 0.04 mS cm⁻¹ at 85°C. The total water content of $[TMDPH_2][SO_4]$ was determined 0.18 ± 0.02 wt-% under ambient humidity and temperature. Although $[TMDPH_2][SO_4]$ was soluble in water, dimethyl sulfoxide, methanol, and acetic acid, it was immiscible with ethanol, acetonitrile, ethyl acetate, acetone, chloroform, dichloromethane, and *n*-hexane at room temperature.

Thermal Behaviour of [TMDPH₂][SO₄]

The thermal behaviour of [TMDPH₂][SO₄] was investigated by a differential scanning calorimetry (DSC) plot in two cycles over temperature ranges of 30–300 and 30–500°C (see Supplementary Material, Fig. S12). DSC of pure TMDP has been previously reported in the literature,^[26] and it displays two sharp and one broad endothermic peak centred at 58, 110, and 332°C. The peaks at 52.3 and 332.5°C were attributed to the melting and boiling points of TMDP, respectively. The second endothermic broad peak at a range of 76–157°C was attributed to the desorption of trapped moisture in TMDP.

Under a nitrogen atmosphere and at a range of 30-300°C, three sharp and one weak endothermic peak(s) were displayed on the DSC curve of [TMDPH2][SO4], and no exothermic peak was observed. The first sharp peak was assigned to the melting of the IL which began at 85.2°C and ended at 111.7°C with a latent heat of fusion of 140.8 J g^{-1} , which was in good agreement with the obtained melting point achieved using an open capillary tube in a Büchi B-545 apparatus (mp 74-75°C). The second endothermic sharp peak was observed in the range 131.3-175.5°C centred at 160.2°C, which was assigned to the dehydration and degassing of the IL with a latent heat of evaporation of 38.0 J g^{-1} . Two sharp peaks were observed at a range of 248.2 to 294.7°C, which were assigned as the boiling point decomposition of [TMDPH₂][SO₄] due to an appreciable loss of weight, a remarkable change in heat capacity of the sample, and an exothermic baseline shift. The latent heat of evaporation and decomposition of the [TMDPH₂][SO₄] were 276.3 and 187.0 J g^{-1} , respectively. There was no exothermic and endothermic peak in the second cycle at a range of 30-500°C, which supports the evaporation/decomposition of the [TMDPH₂][SO₄] below 300°C in the first cycle.

Moreover, the thermal stability of [TMDPH₂][SO₄] was studied in a temperature range from 30 to 800°C under a nitrogen atmosphere through thermogravimetric analysis/differential thermal analysis (TGA/DTA) (see Supplementary Material, Fig. S13). Three peaks were observed on the DTA curve, and [TMDPH₂][SO₄] started to decompose at 270°C, which was in good agreement with the result of DSC. The thermal decomposition was mainly completed at 450°C. The first peak was observed below 200°C with a maximum mass loss of 6.1%; this loss was related to the removal and evaporation of the trapped and adsorbed moisture in [TMDPH₂][SO₄]. The second and third peaks showed a maximum mass loss of 31.5 and 34.4% at 250-290 and 290-330°C, respectively, which were related to the total decomposition of [TMDPH2][SO4]. The DSC and TGA/DTA results showed that [TMDPH₂][SO₄] is thermally stable up to 270°C, probably owing to the strong

Entry	[TMDPH ₂][SO ₄] [mol-%]	Molar ratio of <i>n</i> -butanol to acetic acid	Temp. [°C]	Reaction time [h]	Yield ^A [%]
1	_	1.0:1.0	60	4.0	12
2	5	1.0:1.0	60	4.0	34
3	10	1.0:1.0	60	4.0	42
4	15	1.0:1.0	60	4.0	42
5	10	1.1:1.0	60	4.0	52
6	10	1.2:1.0	60	4.0	58
7	10	1.3:1.0	60	4.0	68
8	10	1.4:1.0	60	4.0	68
9	10	1.3:1.0	65	4.0	72
10	10	1.3:1.0	75	4.0	78
11 ^B	10	1.3:1.0	85	4.0	88
12	10	1.3:1.0	100	4.0	88
13	1.0	1.3:1.0	85	2.0	54
14	1.0	1.3:1.0	85	6.0	81
15	1.0	1.3:1.0	85	8.0	75

Table 2. Optimisation of the esterification of *n*-butanol and glacial acetic acid

^AGC yield.

^BThe chosen optimal conditions.

$$R-OH + H_{3}C + OH + H_{3}C + OH + \frac{[TMDPH_{2}][SO_{4}] (10 \text{ mol-}\%)}{cyclohexane, 75-85^{\circ}C, 4 \text{ h}} + H_{3}C + OH + H_{$$

Scheme 2. Esterification of various alcohols and glacial acetic acid in the presence of [TMDPH₂][SO₄].

electrostatic attractions between the piperidinium cations and the sulfate anion in the structure of the [TMDPH₂][SO₄].

Esterification of Alcohols and Glacial Acetic Acid Using [TMDPH₂][SO₄] as a Catalyst

Initially, the esterification of *n*-butanol (1e) and acetic acid was chosen as a model reaction. The influence of four parameters, including the amount of [TMDPH₂][SO₄], the ratio of *n*-butanol to acetic acid, temperature, and reaction time were studied to find the optimised reaction conditions. As the results show in Table 2, the yield of esterification increased with an increase in the catalyst loading, and the highest yield was observed with 10 mol-% of the catalyst (Table 2, entries 1–4). The most effective molar ratio of *n*-butanol to glacial acetic acid was 1.3 at 60°C within 4 h (Table 2, entries 5–8).

A significant improvement in the yield was observed when the model reaction was carried out at higher temperatures up to 90°C; however, no change occurred in yield at a higher temperature (100°C) (Table 2, entries 9–12). A shorter or longer reaction time of about 4 h resulted in lower yields of the desired product (Table 2, entries 13–15), which can probably be due to the reversibility of the esterification process. Based on our results, entry 11 in Table 2 was selected as the best experimental conditions, i.e., 10 mol-% catalyst, 1.3 : 1.0 molar ratio of *n*-butanol to acetic acid, 85°C, and 4 h reaction time.

The catalytic activity of [TMDPH₂][SO₄] was demonstrated for the esterification of other alcohols and glacial acetic acid under optimised reaction conditions (Scheme 2).

A variety of alcohols were treated with acetic acid under optimised reaction conditions (Table 3). The results showed that the primary alcohols gave higher yields than secondary alcohols, which afforded a slightly higher yield than tertiary alcohols, which can be attributed to the acidity of alcohol (Table 3, entries 1–14). Moreover, competitive dehydration was observed for the secondary and tertiary alcohols under optimised reaction conditions (Table 3, entries 10–14). The substituents at the *ortho*-position of the benzyl alcohols gave lower yields of acetate esters than the same substituents at the *para*-position, which is probably due to the steric effect of the substituents (Table 3, entries 15–22), as well as the hydrogen bond formation between $-NO_2$ and -Cl and the hydroxy group of the benzyl alcohols (Table 3, entries 21 and 22).

The enantioselectivity of the current protocol was investigated through the reaction of glacial acetic acid with (–)-menthol $([\alpha]_D -50 \pm 1^\circ, c \ 10\%$ ethanol, $\ge 99\%$ e.e.) and (+)-borneol $([\alpha]_D +37 \pm 2^\circ, c \ 5\%$ in ethanol, 99% e.e.) under optimal conditions, which gave (–)-menthyl acetate $([\alpha]_D = -80^\circ, in$ benzene, 97% e.e.) and (+)-bornyl acetate $([\alpha]_D = +41^\circ, neat, 96\%$ e.e.) with retention of the configuration at the chiral centre in 72 and 70% yield, respectively (Table 3, entries 11 and 12). The optical rotation of the desired acetates was recorded and reported based on samples from Sigma–Aldrich.

According to a proposed mechanism, the glacial acetic acid is initially activated by [TMDPH₂][SO₄] through hydrogen bond formation (Scheme 3). A nucleophilic attack of the alcohol to the activated acetic acid leads to the formation of intermediate **III**. Hydrogen rearrangement and dehydration of intermediate **III** gives the alkyl acetate. The dehydration step can be promoted by the hygroscopic property of [TMDPH₂][SO₄]. Moreover, the cyclohexane can favour the forward reaction through extraction and separation of the produced alkyl acetate.

The reusability of $[TMDPH_2][SO_4]$ was also studied using the model reaction at optimal conditions, which afforded **2e** in 88–82 % yield over five catalytic cycles.

In another experiment, the model reaction was monitored for a longer reaction time. Aliquots were analysed by gas

Entry ^A	Alcohol 1a-v	Ester 2a–h	Temp. [°C]	Yield ^B [%]
1	CH ₃ OH	2a	75	82 ± 2
2	CH ₃ CH ₂ OH	2b	85	85 ± 2
3	CH ₃ CH ₂ CH ₂ OH	2c	85	88 ± 3
4	(CH ₃) ₂ CHOH	2d	85	85 ± 2
5	CH ₃ CH ₂ CH ₂ CH ₂ OH	2e	85	88 ± 3
6	(CH ₃) ₂ CHCH ₂ OH	2f	85	80 ± 1
7	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH	2g	85	85 ± 2
8	(CH ₃) ₂ CHCH ₂ CH ₂ OH	2h	85	82 ± 2
10	OH	2i	85	75 ± 3
11	OH	2j	85	72 ± 1
12	Ан	2k	85	70 ± 1
13	ОН	21	85	76±2
14	ОН	2m	85	62 ± 3
15	V	20	75	87 + 7
16	4-Me-C ₂ H ₂ -CH ₂ OH	20	75	82 ± 2 83 ± 1
17	4-NO2-C2H4-CH2OH	20 2n	75	85 ± 1 85 ± 3
18	4-Cl-CzH4-CH2OH	20	75	83 ± 3 83 ± 2
19	$2-MeO-C_4H_4-CH_2OH$	2r	75	$\frac{05 \pm 2}{78 + 2}$
20	$2-\text{Me-C}_{2}\text{H}_{4}-\text{CH}_{2}\text{OH}$	25	75	76 ± 2 76 ± 1
21	$2-NO_2-C_2H_4-CH_2OH$	2t	75	70 ± 1 74 + 1
22	2-Cl-C/H4-CH2OH	2v	75	75 ± 1
	2-01-06114-0112011	<u> </u>	15	/ J ± 1

Table 3. Esterification of various alcohols and glacial acetic acid in the presence of [TMDPH₂][SO₄] under optimised reaction conditions

^AReaction conditions: alcohol **1a–v** (0.13 mol), glacial acetic acid (0.1 mol), cyclohexane (1.5 mL), [TMDPH₂][SO₄] (0.01 mmol), reaction time (4 h). ^BGC-MS yield. The esterification reactions were carried out in triplicate and conducted at least twice on separate days.



Scheme 3. A schematic reaction mechanism of the esterification in the presence of [TMDPH₂][SO₄].



Scheme 4. Esterification of α-tocopherol (α-TCP) with glacial acetic acid using [TMDPH₂][SO₄].

Table 4. Catalytic efficiency of five ionic liquid catalysts for the esterification of n-butanol and glacial acetic acid

Entry ^A	Ionic liquid	Reaction time [min]	Yield ^B [%]
1	TMDPS	230	85 ± 2
2	[TEA][HSO ₄]	240	80 ± 2
3	[MIm-C4-MIm][HSO ₄] ₂	180	88 ± 2
4	[Im-C4-Im(SO ₃ H) ₂] ₂ Cl	200	85 ± 2
5	[TMDPH ₂][SO ₄]	240	85 ± 2

^AReaction conditions: *n*-butanol (0.13 mol), glacial acetic acid (0.1 mol), cyclohexane (1.5 mL), ionic liquid (0.01 mmol). ^BGC-MS yield.

chromatography–mass spectrometry (GC-MS) at intervals of 1 h, while the stirring of the reaction mixture continued under optimised reaction conditions. Complete (100 %) conversion of glacial acetic acid was observed after 430 ± 10 min.

Finally, the esterification of α -tocopherol (a-TCP) was conducted to show the potential of the current method for a scale-up application. It is well known that tocopherols, an isoform of vitamin E, are sensitive to light and air. Their antioxidant efficiency is rapidly reduced,^[30] while their ester isoforms exhibited moderate to good stability to light and air.^[31] Large scale acetylation of α -tocopherol (a-TCP) (20 mmol) with glacial acetic acid (30 mmol) was carried out using [TMDPH₂] [SO₄] (10 mol-%) at 60°C, which gave 8.11 g (88.4 % yield) after 4 h incubation in the absence of light under N₂ atmosphere (Scheme 4).

Very recently, our group reported the synthesis, characterisation, and catalytic application of a low viscous ionic liquid, namely 4,4'-trimethylene-N,N'-sulfonic acid-dipiperidinium chloride (TMDPS).^[32] We investigated the structure–activity relationship of the two ionic liquids [TMDPH₂][SO₄] and TMDPS on the model esterification. The model reaction was also carried out using 10 mol-% of TMDPS, 1,1'-butylenebis-(3-sulfo-3*H*-imidazol-1-ium) chloride ([Im-C4-Im(SO₃H)₂]₂₋ Cl), 1,1'-butylenebis(3-methyl-3*H*-imidazol-1-ium) dihydrogensulfate ([MIm-C4-MIm][HSO₄]₂), and triethylammonium hydrogen sulfate ([TEA][HSO₄]). The ILs were fabricated according to the literature methods.^[7,25,32–33] Although the five ILs can be interchanged under appropriate conditions, the ILs that contained two sulfonic acid moieties or two acidic anions, namely hydrogen sulfate, showed higher yields within shorter reaction times (Table 4, entries 1, 3, and 4). The anion and cation effect for [TMDPH₂][SO₄] and [TEA][HSO₄] on the yield and rate are negligible within experimental error in the measurements (Table 4, entries 2 and 5).

Experimental

General

Unless specified, all chemicals were of analytical grade and purchased from Merck, Aldrich, and Fluka Chemical Companies and used without further purification. The FT-IR spectra were recorded on a Perkin Elmer RX1 FT-IR spectrophotometer in the range of $4000-400 \text{ cm}^{-1}$. The amount of water in the liquid salt was determined by Karl Fisher (KF) titration, using a Metrohm 831 kF coulometer in conditions of ambient humidity and room temperature. The ionic conductivity (σ) was measured using a Mettler Toledo Seven Easy conductivity meter at 25°C. The ¹H and ¹³C NMR spectra were recorded with Bruker Avance 600 and 400 MHz instruments. All chemical shifts are quoted in parts per million (ppm) relative to TMS using a deuterated solvent. DSC curves were obtained with the use of a DSC-Mettler Toledo DSC 822e calorimeter. The measurements were performed in aluminium pans with a pierced lid with a sample mass 9.24 mg under a dry nitrogen gas atmosphere (10 mL min^{-1}) . Dynamic scans were performed at a heating rate of 10°C min⁻¹ in two temperature cycles at a range of 30-300 and 30-500°C. TGA/DTA curves were obtained with the use of a Mettler Toledo TGA/ SDTA 851e. All measurements were performed in an Al₂O₃ crucible with a sample mass of 10.65 mg under a nitrogen atmosphere (10 mL min⁻¹). Dynamic scans were performed at a heating rate of 10° C min⁻¹ in the temperature range of $30-800^{\circ}$ C. The purity and yield of the products were determined using GC-MS on an Agilent 6890GC/5973MSD analysis instrument under 70 eV conditions. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. Positive and negative ion ESI-MS analyses were performed using an Agilent 6560 iFunnel Q-TOF LC-MS instrument.

Synthesis using TMDP and Sufuric Acid at a Ratio of 1:1

A flask containing a solution of 4,4'-trimethylene-dipiperidine (4.21 g, 20 mmol) in dry CH₂Cl₂ (20 mL) was cooled to a low temperature by an ice bath. Sulfuric acid (98 %, 1.840 g mL⁻¹) (1.1 mL, ~20 mmol) was added dropwise to the solution at low temperature (ice bath). Two phases were formed after stirring at room temperature overnight. After the decantation of the upper phase, the white waxy residue was washed with CH₂Cl₂ (3 × 10 mL), and excess solvent was removed by a rotary evaporator under vacuum. The obtained white solid was crystallised from methanol.

Synthesis of [TMDPH₂][SO₄]

A flask containing a solution of 4,4'-trimethylene-dipiperidine (4.21 g, 20 mmol) in dry CH₂Cl₂ (20 mL) was cooled to a low

temperature by an ice bath. Sulfuric acid (98 %, 1.840 g mL⁻¹) (2.18 mL, ~40 mmol) was added dropwise to the solution at low temperature (ice bath). Two phases were formed after stirring at room temperature overnight. The upper phase was removed by decantation, and the pale yellow sticky residue was washed with CH_2Cl_2 (3 × 10 mL). After evaporation of excess solvent under reduced pressure, the resulting IL was obtained as a pale yellow sticky solid. The IL could be crystallised from methanol.

Typical Esterification Procedure

Glacial acetic acid (0.600 g, 0.572 mL, 10 mmol), *n*-butanol (9.694 g, 11.968 mL, 13 mmol), $[\text{TMDPH}_2][\text{SO}_4]$ (0.308 g, 1.0 mmol), and cyclohexane (1.157 g, 15 mL) were taken into a 25 mL three necked flask. The flask was equipped with a manifold and a condenser. After an appropriate reaction time (4 h), a liquid bi-phase formed in the flask. The liquid phase containing the ester was isolated by separating funnel and was analysed by GC-MS. [TMDPH_2][SO_4] was isolated after removing the product and water by separating funnel and drying in a vacuum oven at 50°C overnight before being tested for reusability.

Esterification of *α*-TCP with Glacial Acetic Acid

 α -TCP (20 mmol), glacial acetic acid (30 mmol), and [TMDPH₂] [SO₄] (0.616 g) were mixed and stirred at 60°C under N₂ atmosphere for 2 h in a 100 mL round bottom flask covered with tin foil. Liquid chromatography–mass spectrometry was utilised to determine the purity and yield of *O*-acetyl- α -tocopherol (Ac-TCP) using vitamin E acetate (96% Sigma–Aldrich) as an external standard. The identification of Ac-TCP was performed by comparison of its NMR data with the reference compound.^[34] The yield of Ac-TCP was also calculated based on a reported equation in the literature.^[35]

Conclusion

In conclusion, a novel bis-core dicationic TMDP salt containing a sulfate counterion was synthesised, and its chemical structure was elucidated by FT-IR, 1D and 2D NMR, and mass analyses. Some physical properties and thermal behaviour and thermal stability of the new IL were recorded and investigated. The structure elucidation showed that the new IL is a diprotic acid like sulfuric acid, which can be used as a safe alternative of sulfuric acid. The catalytic activity of [TMDPH2][SO4] was employed to promote the esterification process under mild conditions. A simple experimental and sustainable procedure, high yield of the desired product, simple workup, and reusability of catalyst are some of the merits of the current protocol. Another superiority of the new method is avoiding and reducing heavy metal and corrosive waste generation. Further research is being conducted in our group to investigate new applications of TMDP and sulphuric acid at a ratio of 1 : 1 and 1 : 2 with promising results.

Supplementary Material

Supplementary data to this article is available on the Journal's website.

Conflicts of Interest

The authors declare no conflicts of interest.

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