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FULL PAPER

Synthesis and characterization of a novel organic–inorganic hybrid salt and its application as a highly effectual Brønsted–Lewis acidic catalyst for the production of *N*,*N*′-alkylidene bisamides

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In this research, a novel organic–inorganic hybrid salt, namely, N^1,N^1,N^2,N^2-tetramethyl-N^1,N^2-bis(sulfo)ethane-1,2-diaminium tetrachloroferrate ([TMBSED][$FeCl_4$]$_2$) was prepared and characterized by Fourier-transform infrared spectroscopy (FT-IR), energy-dispersive X-ray spectroscopy (EDX), elemental mapping, field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), thermal gravimetric (TG), differential thermal gravimetric (DTG), and vibrating-sample magnetometry (VSM) analyses. Catalytic activity of the hybrid salt was tested for the synthesis of *N*,*N*′-alkylidene bisamides through the reaction of benzamide (2 eq.) and aromatic aldehydes (1 eq.) under solvent-free conditions in which the products were obtained in high yields and short reaction times. The catalyst was superior to many of the reported catalysts in terms of two or more of these factors: the reaction medium and temperature, yield, time, and turnover frequency (TOF). [TMBSED][$FeCl_4$]$_2$ is a Brønsted–Lewis acidic catalyst; there are two SO_3H groups (as Brønsted acidic sites) and two tetrachloroferrate anions (as Lewis acidic sites) in its structure. Highly effectiveness of the catalyst for the synthesis of *N*,*N*′-alkylidene bisamides can be attributed to synergy of the Brønsted and Lewis acids and also possessing two sites of each acid.

KEYWORDS
Brønsted–Lewis acidic catalyst, *N*,*N*′-alkylidene bisamide, N^1,N^1,N^2,N^2-tetramethyl-N^1,N^2-bis(sulfo)ethane-1,2-diaminium tetrachloroferrate ([TMBSED][$FeCl_4$]$_2$), organic–inorganic hybrid salt, solvent-free

1 | INTRODUCTION

Organic–inorganic hybrid material is generally defined as a compound in which the structure is formed from organic and inorganic components interacting with each other at the molecular scale. This can be occurred by weak interactions such as hydrogen bonding, van der Waals forces, and electrostatic interactions or through strong coordinative, covalent, and ionic bonds.[1] It is worth note that characteristics of the hybrid materials are not only sum of their organic and inorganic constituents properties but also related to the nature of the interfaces and the ratio of each moiety.[2] A significant class of these compounds involves organic–inorganic hybrid salts.[3] The hybrid materials have several unbeatable advantages, consisting of eco-friendly nature, designable for a variety of applications, effectiveness, appropriate thermal and chemical stability, noncorrosiveness, and simple isolation from the process reactor. They have various applications in pharmaceutical and industrial fields; for example, they have been applied as semiconductor,[4] sensors,[5] and photodetector[6] and in fluid–fluid separations,[7] cancer therapy,[8] luminescence studies,[9] and optical devices.[10] Organic–inorganic hybrid materials have been also employed as efficient catalysts in synthetic organic chemistry.[11–19]

Bisamide functional group can be found in the scaffold of a wide range of biologically, pharmaceutically, and industrially important compounds.[20–31] Bisamides have been used as ligands for the preparation of biologically active compounds in the Ullmann reaction[20] and as essential moieties to introduce *gem*-diaminoalkyl groups in retro-inverse pseudo-peptide materials.[21] These compounds have been utilized in the synthesis of peptidomimetic compounds.[22] Bisamide-containing compounds have been also applied as drug release,[23] antitumor,[24] anti-inflammatory,[25] and antimicrobial[25] agents. Moreover, bisamides coordinated with metal ions have been utilized for bimodal (optical/magnetic resonance) imaging,[26] magnetic resonance imaging (MRI) blood-pool contrasting,[27] and removal of organic dyes[28] and as inhibitor against α-glucosidase[29] and reagents in organic synthesis.[30,31] A kind of these compounds is *N*,*N′*-alkylidene bisamides, which has been synthesized through the reaction of primary amides (2 eq.) and aldehydes (1 eq.); some catalysts have been reported to perform this transformation, for example, KH_2PO_4 supported on silica from rice husk ash (H_2PO_4@RHA),[32] $H_{14}[NaP_5W_{29}MoO_{110}]$,[33] sulfonated carbon/nano-titania composite (C/TiO_2-SO_3H),[34] hydroxyapatite,[35] ZnO/KIT-6@$NiFe_2O_4$,[36] nano-2-[*N′*,-*N′*-dimethyl-*N′*-(silica-*n*-propyl)ethanaminium chloride]-*N*,*N*-dimethylaminium bisulfate (nano-[DSPECDA][HSO_4]),[37] montmorillonite K10,[38] $NiFe_2O_4$@SiO_2-PPA,[39] 3D-network polymer-supported ionic liquid,[40] molybdate sulfuric acid (MSA),[40] silica sulfuric acid (SSA),[41] and graphene oxide anchored with sulfonic acid-functionalized glycerin (GO@Gl-SO_3H).[42]

Solvent-free condition is a practical, well-known, useful, and green technique that has been used in organic synthesis; its advantages have been mentioned in the literature.[43–45]

Considering the high significance of organic–inorganic hybrid materials and *N*,*N′*-alkylidene bisamides, herein, a novel organic–inorganic hybrid salt, namely, N^1,N^1,N^2,N^2-tetramethyl-N^1,N^2-bis(sulfo)ethane-1,2-diaminium tetrachloroferrate ([TMBSED][$FeCl_4$]$_2$) has been synthesized and characterized by Fourier-transform infrared spectroscopy (FT-IR), energy-dispersive X-ray spectroscopy (EDX), elemental mapping, field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), thermal gravimetric (TG), differential thermal gravimetric (DTG), and vibrating-sample magnetometry (VSM) analyses. Then, it has been used as a highly effectual Brønsted–Lewis acidic catalyst for the preparation of *N*,*N′*-alkylidene bisamides through the reaction of benzamide (2 eq.) with aromatic aldehydes (1 eq.) under solvent-free and green conditions.

2 | EXPERIMENTAL SECTION

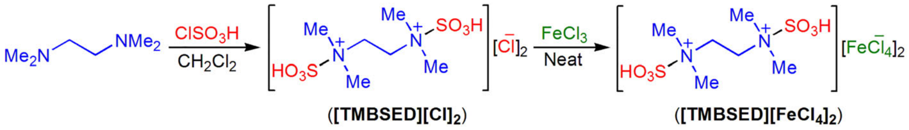
2.1 | Materials and instruments

All reactants and solvents were purchased from Merck or Fluka Chemical Companies. Identification of the known products was done by comparing their melting points and/or spectral data with the reported data. Observing the reactions progress was achieved by thin-layer chromatography (TLC) using silica gel SIL G/UV 254 plates. The nuclear magnetic resonance (NMR) spectra were run on a Bruker Avance DPX FT-NMR spectrometer (δ in ppm). Melting points were measured on a Buchi B-545 instrument in open capillary tubes. FT-IR spectrums were recorded by a Shimadzu IR-60 instrument. EDX and mapping analysis were done by a SAMX-EDS apparatus (France system). The morphologies and sizes of the particles were characterized by FE-SEM, model MIRA3TESCAN-XMU. The XRD analysis was carried out using a device model: X'Pert PRO MPD, PANalytical, the Netherlands (Cu Kα radiation, $\lambda = 1.5408$). Thermal gravimetric analysis (TGA) was performed by a Bahr STA 504 instrument (Germany), at 25–600°C, with temperature increment rate of 10°C min^{-1} in argon atmosphere.

2.2 | The synthesis of [TMBSED][$FeCl_4$]$_2$

A solution of N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine (5 mmol, 0.581 g) in dry CH_2Cl_2 (20 mL) was added dropwise to a stirring solution of chlorosulfonic acid (10 mmol, 1.165 g) in dry CH_2Cl_2 (20 mL) over a period of 10 min, at 10°C, and the resulting solution was stirred for 4 h at room temperature. Afterward, the solvent was evaporated; the liquid residue was triturated with dry petroleum ether (3 × 2 mL) and dried under vacuum at 90°C to produce [TMBSED][Cl]$_2$.[46,47] Finally, $FeCl_3$ (10 mmol, 1.622 g) was gradually added to [TMBSED][Cl]$_2$ (5 mmol, 1.746 g) and stirred for 2 h at room temperature and 12 h at 70°C to afford [TMBSED][$FeCl_4$]$_2$ (Scheme 1).

SCHEME 1 The synthesis of [TMBSED][FeCl$_4$]$_2$



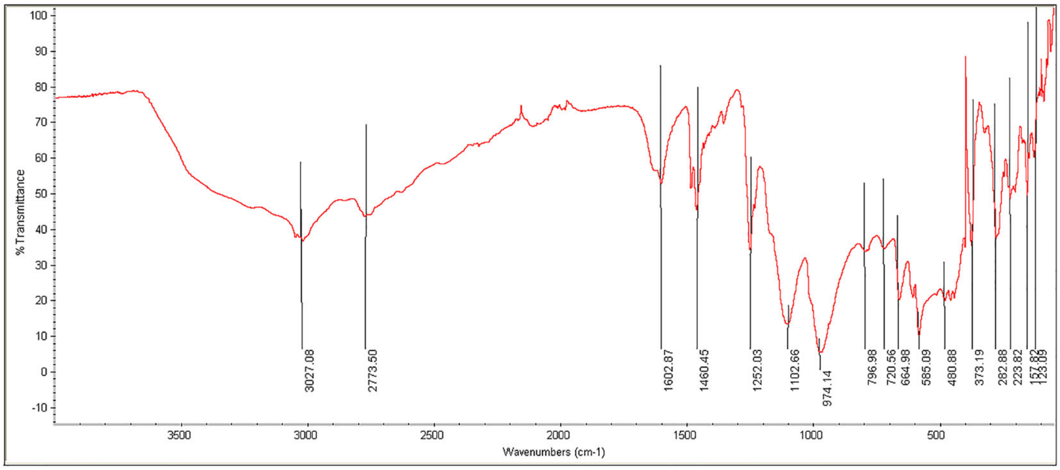


FIGURE 1 The FT-IR spectrum of [TMBSED][FeCl$_4$]$_2$

2.3 | General procedure for the preparation of *N,N′*-alkylidene bisamides

A mixture of banzamide (2 mmol, 0.242 g), aldehyde (1 mmol), and [TMBSED][FeCl$_4$]$_2$ (0.1 mmol, 0.067 g) was strongly stirred by a small rod at 80°C. When TLC showed consuming the reactants, the reaction mixture was cooled to room temperature; EtOAc (10 mL) was added and stirred for 2 min under reflux conditions; the insoluble catalyst was isolated by centrifuging and decanting (the catalyst was washed by EtOAc [2 × 3 mL] and dried). The EtOAc obtained from the decanting was distilled, and the remainder solid was recrystallized from EtOH (95%) to give the pure product. [TMBSED][FeCl$_4$]$_2$ was reusable for one time.

TABLE 1 The FT-IR data of [TMBSED][FeCl$_4$]$_2$

Adsorption (cm^{-1})	Bond or functional group
~3,650–2,000	Stretching of OH groups of SO_3H
1,460	Bending of C–H
1,252	Stretching of C–N
1,103	Symmetric stretching of $-SO_2-$
721	Symmetric of S–O
585	Bending of $-SO_2-$
373	Fe–Cl of tetrachloroferrate
283	Fe–Cl of tetrachloroferrate
123	Cl–Fe–Cl of tetrachloroferrate

Abbreviation: FT-IR, Fourier-transform infrared spectroscopy.

Note: Selected spectral data and original spectrums of the synthesized bisamides have been presented in supporting information (Figures S1–S6).

3 | RESULTS AND DISCUSSION

3.1 | The catalyst characterization

The novel organic–inorganic hybrid salt, N^1,N^1,N^2,N^2-tetramethyl-N^1,N^2-bis (sulfo)ethane-1,2-diaminium tetrachloroferrate ([TMBSED][FeCl$_4$]$_2$), was characterized by FT-IR, EDX, elemental mapping, FE-SEM, XRD, TG, DTG, and VSM techniques.

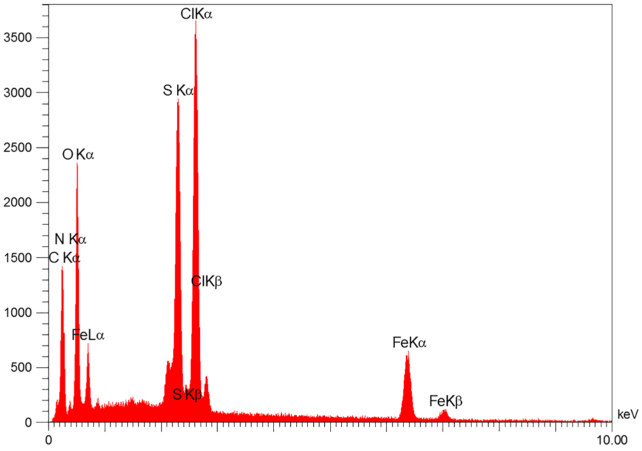


FIGURE 2 The EDX spectrum of [TMBSED][FeCl$_4$]$_2$

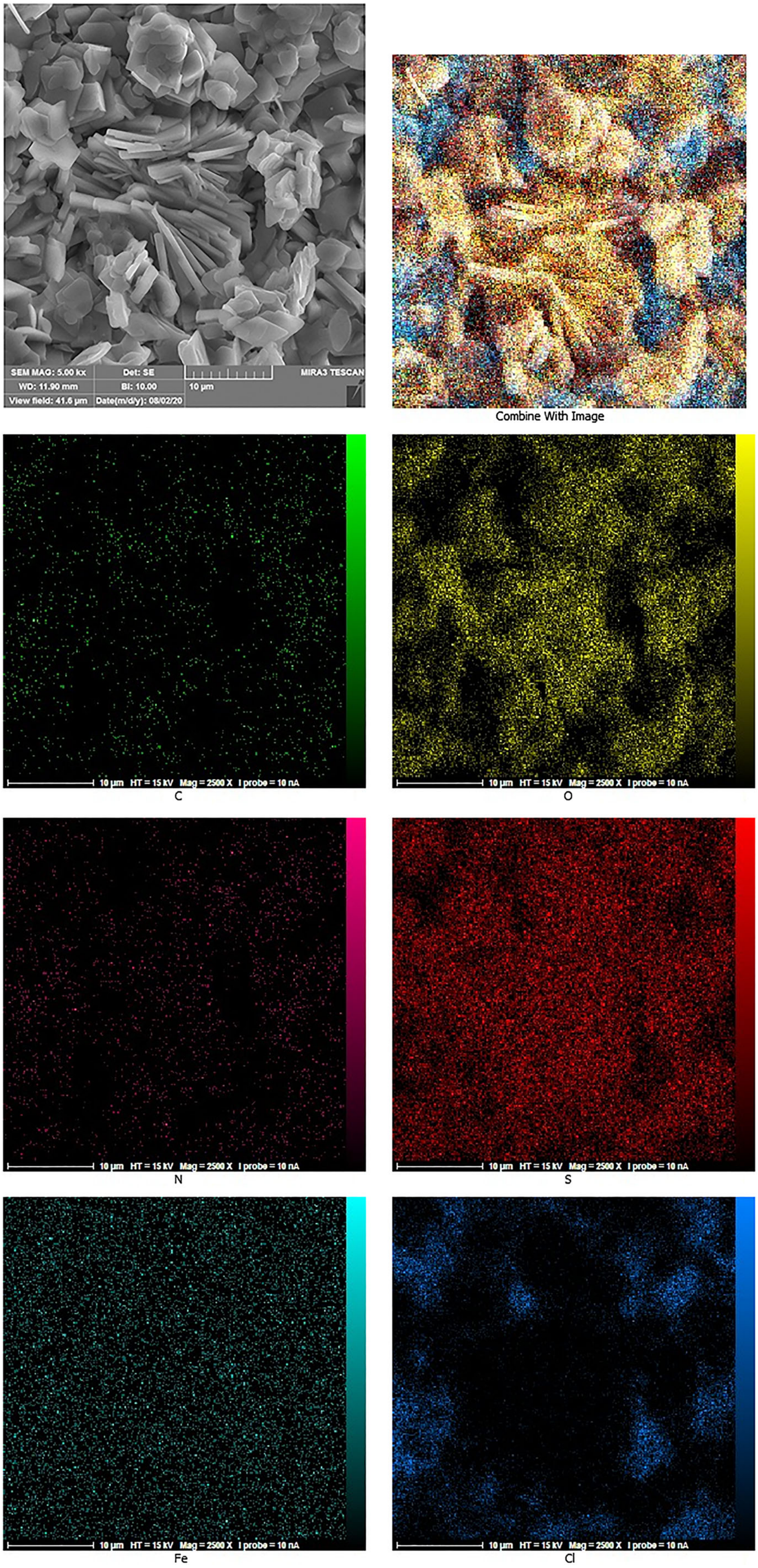


FIGURE 3 Elemental mapping analysis of the catalyst

The FT-IR spectrum of [TMBSED][FeCl$_4$]$_2$ is presented in Figure 1, and the related adsorptions to each bond and functional group are shown in Table 1. The peaks corresponded to all expected bonds or functional groups in the cation and anion of the hybrid salt were observed in the spectrum. The interpretation of the FT-IR spectral data is in accordance with the literature data.[12,46–49]

Existing all expected elements (C, O, N, S, Fe, and Cl) in the structure of the organic–inorganic hybrid material were verified by EDX; no extra element was observed in the spectrum (Figure 2). Presence of carbon, oxygen, nitrogen, sulfur, iron, and chlorine elements in the structure of [TMBSED][FeCl$_4$]$_2$ was also confirmed by elemental mapping analysis, as shown in Figure 3.

The FE-SEM images of [TMBSED][FeCl$_4$]$_2$ are illustrated in Figure 4. As it can be seen in Figure 3, most of the particles sizes were micro (105–171 nm), and a few of them were nano (86–96 nm).

The XRD pattern of the catalyst (Figure 5) indicated several sharp peaks at $2\theta \approx 8.8$, 9.8, 13.4, 16.0, 17.2, 18.9, 21.3, 22.0, 25.2, 26.9, 28.8, 30.5, 38.6, 39.5, 43.2, 44.9 and a few broad peaks (relatively) at $2\theta \approx 50.7$–53.0, 53.0–55.0, 57.6–60.2°. According to these results, most of the particles have crystalline form, and some of them have amosphorous form. The chemical sources confirmed these interpratations.[12,19]

Thermal stability of [TMBSED][FeCl$_4$]$_2$ was determined by TGA. Considering the TG diagram (Figure 6), the organic–inorganic hybrid salt showed proper thermal stability, and main weight losses (decomposition) were occurred after about 205°C. Thus, it can be utilized as catalyst for organic transformations that need high temperature to perform. The weight losses were occurred in three steps. The first weight loss ($\sim$11.5%) below about 172°C (with $T_{\max}$ at 121°C in DTG plot) can be attributed to evaporation of adsorbed water and other solvents by [TMBSED][FeCl$_4$]$_2$. The second and third weight losses ($\sim$56%) were happened at about 172–425°C (with $T_{\max}$ at 242°C in DTG plot) and 425–550°C (with $T_{\max}$ at 507°C in DTG plot), respectively, and may be due to loss of SO_3, $NHMe_2$, and $CH_2{=}CH_2$ from the organic moiety, conversion of tetrachloroferrate to ferric chloride, and oxidation of tetrachloroferrate by oxygen of SO_3. The interpretations were achieved considering the literature.[11,12,50–52]

Magnetic property of N^1,N^1,N^2,N^2-tetramethyl-N^1,N^2-bis(sulfo)ethane-1,2-diaminium tetrachloroferrate was determined by a vibrating sample magnetometer at room temperature; the VSM plot is demonstrated in Figure 7. A linear plot was observed for our catalyst, indicating the paramagnetic property (a paramagnetic material is weakly attracted by an external magnetic field and forms internal induced magnetic fields in the direction of the external applied magnetic field).[50,53]

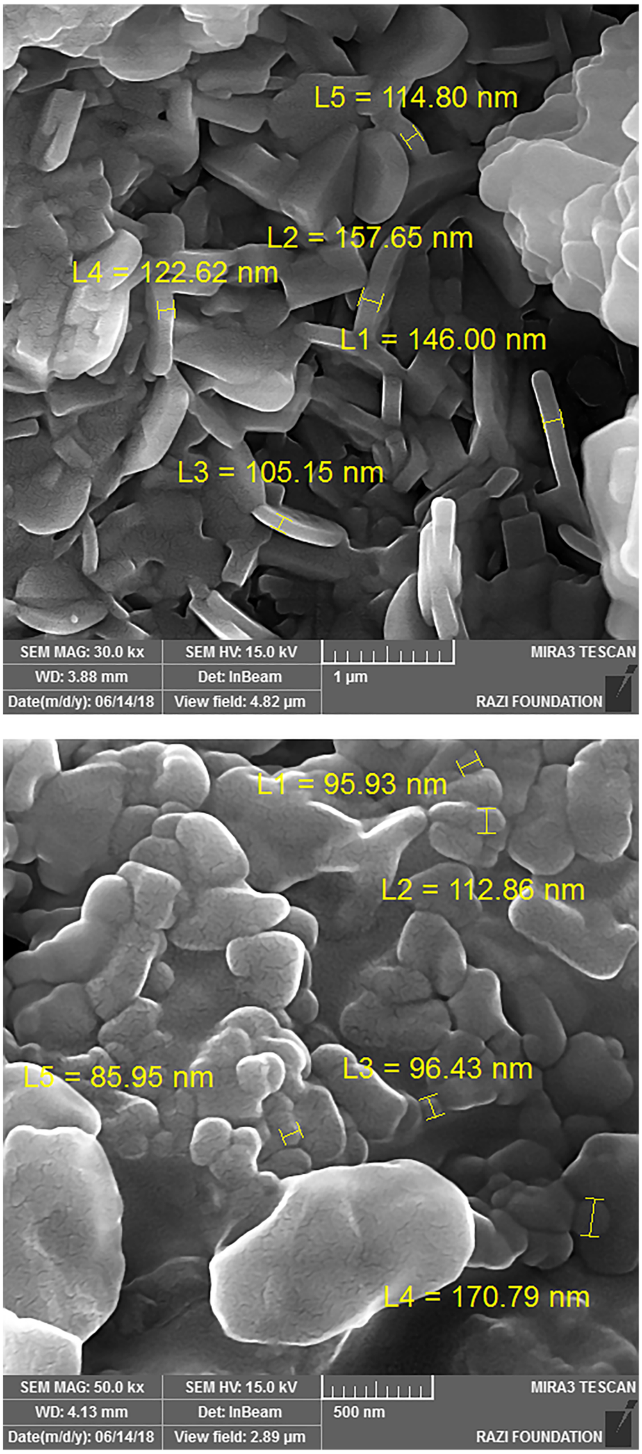


FIGURE 4 The FE-SEM images of [TMBSED][FeCl$_4$]$_2$

3.2 | Catalytic activity of [TMEDSA][FeCl$_4$]$_2$

Catalytic activity of [TMBSED][FeCl$_4$]$_2$ was investigated for the synthesis of *N*,*N*′-alkylidene bisamides. To find the optimal reaction conditions, the condensation of banzamide (2 mmol) and 3-nitrobanzaldehyde (1 mmol) was

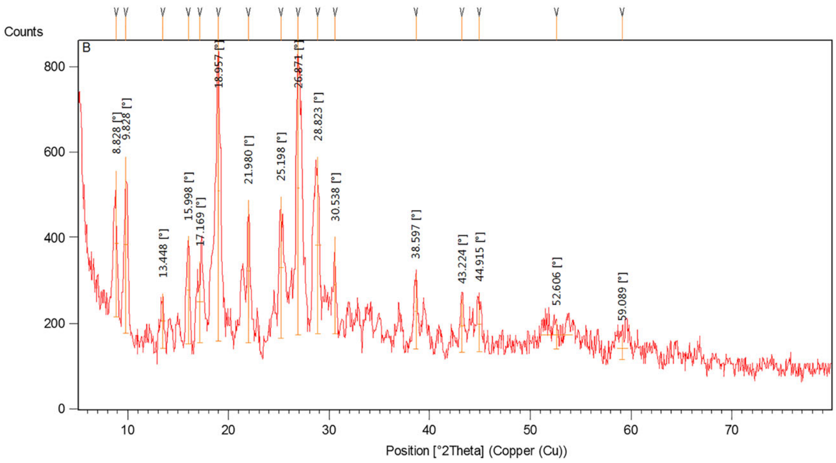


FIGURE 5 The XRD pattern of [TMBSED][$FeCl_4$]$_2$

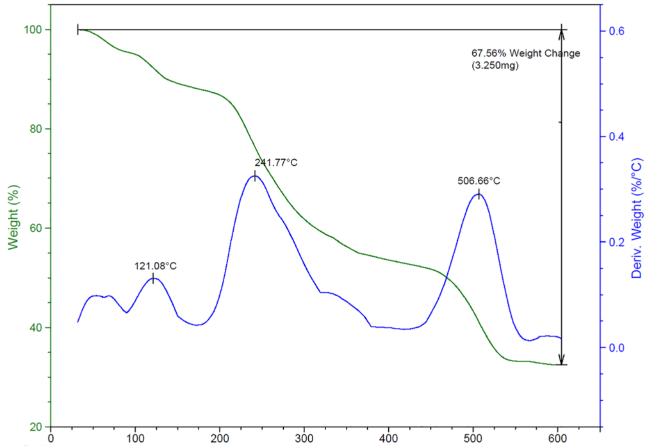


FIGURE 6 The TG and DTG diagrams of [TMBSED][$FeCl_4$]$_2$

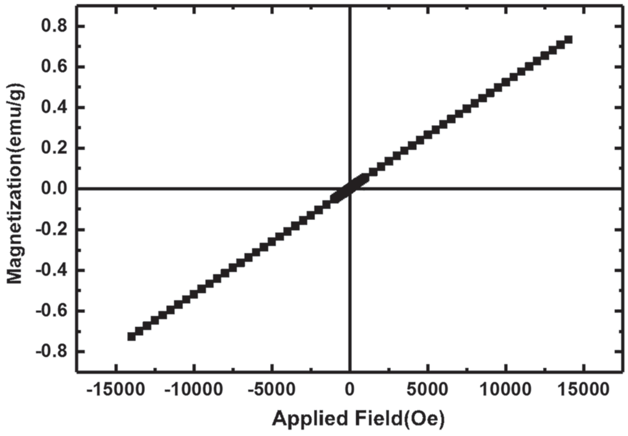
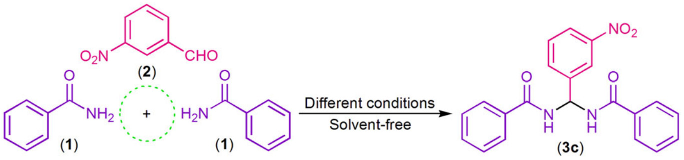


FIGURE 7 The VSM diagram of the hybrid salt

chosen as a model reaction (Scheme 2). The reaction was examined in the presence of different amounts of [TMBSED][$FeCl_4$]$_2$ (5–12 mol%) at a temperature range of 70–90°C under solvent-free conditions. The best results were obtained at 80°C using 10 mol% of the catalyst (the reaction time: 10 min; yield: 96%). Increasing the catalyst amount up to 12 mol% and the temperature up to 90°C has no significant effect on the reaction time and yield.

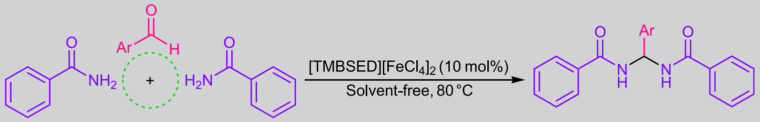
To determine generality and effectiveness of [TMBSED][$FeCl_4$]$_2$ in the preparation of *N*,*N*′-alkylidene bisamides, the condensation of benzamide with different aromatic aldehydes (containing electron-withdrawing, electron-donating, and halogen groups) was examined under the optimal conditions. The obtained reaction times, yields, and turnover frequencies (TOFs) are represented in Table 2. In all cases, the corresponding *N*,*N*′-alkylidene bisamides were obtained in high yields, short times, and good TOF. Additionally, all products were cleanly purified by recrystallization from hot ethanol (95%) and without use of column chromatography.

Considering the literature[32,37,54] and Brønsted–Lewis acidity of [TMBSED][$FeCl_4$]$_2$, a plausible mechanism was proposed for the preparation of *N*,*N*′-alkylidene bisamides (Scheme 3). At first, carbonyl group of the aldehyde is activated by the Brønsted and Lewis acidic moieties of the catalyst (SO_3H and tetrachloroferrate) and then NH_2 group of benzamide performed a nucleophilic attack to the activated carbonyl to provide intermediate **I**. The Brønsted and Lewis acidic sites of the hybrid material accelerate removing a H_2O molecule from **I** to obtain intermediate **II**. Michael-type addition of benzamide to the activated **II** (by the SO_3H and tetrachloroferrate groups of the catalyst) gives **III**. Tautomerization of intermediate **III** by aid of [TMBSED][$FeCl_4$]$_2$ produces the bisamide. Lewis acidity of tetrachloroferrate-bearing catalysts has been mentioned in the literature.[54] The highly effectuality of [TMBSED][$FeCl_4$]$_2$ can be related to its Brønsted–Lewis acidic property (which all steps of the reaction catalyze by both Brønsted and Lewis acidic sites) and also possessing two sites of each acid.



SCHEME 2 The model reaction for optimization of conditions

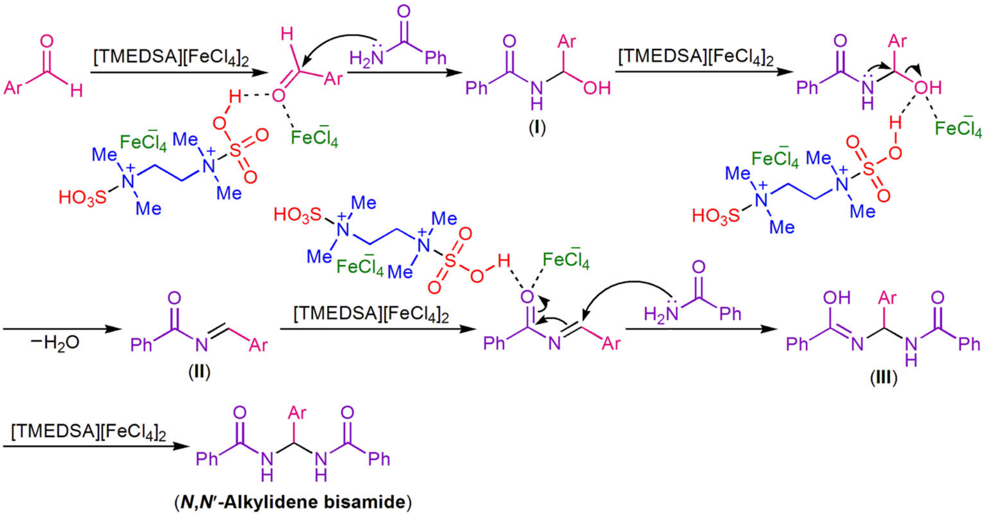
TABLE 2 The production of *N*,*N′*-alkylidene bisamide derivatives using [TMBSED][FeCl$_4$]$_2$



Product	Ar	Time (min)	Yield[a] (%)	TOF (min^{-1})	M.p. °C, measured (reported)
3a	C_6H_5	20	94	0.47	216–218 (218–219)[32]
3b	4-$O_2NC_6H_4$	20	92	0.46	261–263 (259–261)[37]
3c	3-$O_2NC_6H_4$	10	96	0.96	228–230 (228–230)[32]
3d	2-$O_2NC_6H_4$	25	90	0.36	252–254 (255–257)[37]
3e	4-$MeOC_6H_4$	25	89	0.36	224–226 (223–225)[37]
3f	3-$MeOC_6H_4$	20	93	0.47	190–192 (193–195)[32]
3g	4-MeC_6H_4	15	92	0.61	237–239 (240–241)[32]
3h	4-FC_6H_4	25	96	0.38	206–208 (207–209)[38]
3i	4-BrC_6H_4	10	93	0.93	255–257 (256–258)[32]
3j	4-ClC_6H_4	15	97	0.65	256–258 (252–254)[33]
3k	2-ClC_6H_4	20	95	0.48	239–241 (241–242)[36]
3l	2,4-$Cl_2C_6H_3$	20	94	0.47	194–196 (192–194)[32]

[a]Isolated yield (most of the reactions were completed; that is, all the reactants were consumed, and only one desired product was obtained).
Abbreviation: TOF, turnover frequency.

SCHEME 3 The proposed mechanism for the production of *N*,*N′*-alkylidene bisamides



In another study, the results and reaction conditions of [TMBSED][FeCl$_4$]$_2$ for the production of *N*,*N′*-alkylidene bisamides were compared with those of the reported catalysts (Table 3). As the data of Table 3 illustrate, [TMBSED][FeCl$_4$]$_2$ was superior with the other catalysts in terms of two or more of these

TABLE 3 Comparing the reaction conditions and the results of [TMBSED]$[FeCl_4]_2$ with those in the reported catalysts for the production of *N*,*N*′-alkylidene bisamides

Catalyst	Conditions	Time (min)	Yield (%)	TOF (min^{-1})	Ref.
[TMBSED]$[FeCl_4]_2$	Solvent-free, 80°C	10–25	89–97	0.36–0.96	This work
H_2PO_4@RHA	Solvent-free, 80°C	15	71–96	–[a]	Saadati-Moshtaghin[32]
$H_{14}[NaP_5W_{29}MoO_{110}]$	MeOH, reflux	50–150	74–95	0.56–3.80	Maleki et al.[33]
C/TiO_2-SO_3H	Solvent-free, 100°C	30–180	85–94	0.08–0.44	Kour and Paul[34]
Hydroxyapatite	MeOH, reflux	180	87–95	0.10–0.11	Ramachandran et al.[35]
$NiFe_2O_4$@KIT-6@ZnO	Solvent-free, 60°C	10	75–97	–[a]	Saadati-Moshtaghin et al.[36]
Nano-[DSPECDA]$[HSO_4]$	Solvent-free, 90°C	15–30	79–98	1.20–2.97	Zare et al.[37]
Montmorillonite K10	Solvent-free, 100°C	27–180	71–85	–[a]	Lambat et al.[38]
$NiFe_2O_4$@SiO_2-PPA	MeOH, reflux	40–130	52–93	–[a]	Maleki and Baghayeri[39]
Polymer-supported Brønsted acid ionic liquid	Toluene, reflux	20–50	79–92	0.22–0.46	Mouradzadegun et al.[40]
MSA	EtOAc, 80–90°C	25–40	85–91	0.22–0.36	Tamaddon et al.[41]
SSA	EtOAc, 80–90°C	25–45	85–90	–[a]	Tamaddon et al.[41]
GO@Gl-SO_3H	Solvent-free, 110°C	10–25	88–96	–[a]	Naeim-Fallahiyeh et al.[42]

[a] In this research, amount of the active site of the catalyst has not been determined; thus, it was not possible to calculate TOF.
Abbreviation: TOF, turnover frequency.

factors: the reaction medium (performing the synthesis under solvent-free conditions or in toxic solvents), temperature, yield, time, and TOF.

4 | CONCLUSIONS

Briefly, a novel organic–inorganic hybrid salt was introduced as a Brønsted–Lewis acid catalyst for organic synthesis; N^1,N^1,N^2,N^2-tetramethyl-N^1,N^2-bis(sulfo)ethane-1,2-diaminium tetrachloroferrate can catalyze organic reactions that require acidic catalysts. In this study, the synthesis of *N*,*N*′-alkylidene bisamides has successfully catalyzed by the hybrid salt; this synthesis has the following advantages: effectuality, generality, application of solvent-free conditions, high yields, short reaction times, goot TOF, simplicity (procedure, workup, and purification of the products), good agreement with green chemistry principles, usage of a Brønsted–Lewis acid catalyst, easy preparation of the catalyst, and superiority of [TMBSED]$[FeCl_4]_2$ relative to many reported catalysts.

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AUTHOR CONTRIBUTIONS

Abdolkarim Zare: Investigation; project administration; supervision. **Fatemeh Monfared:** Investigation; methodology; software. **Seyed Sajad Sajadikhah:** Investigation; project administration; supervision.

CONFLICT OF INTEREST

There are no conflicts to declare.

DATA AVAILABILITY STATEMENT

All data have been given in the article and supporting information.

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REFERENCES

[1] S. Montes, H. Maleki, *Colloidal Metal Oxide Nanoparticles: Synthesis, Characterization and Applications*, S. Thomas, A.T. Sunny, P. Velayudhan (Ed.), Elsevier: Amsterdam, **2020**. https://doi.org/10.1016/C2016-0-03725-7

[2] C. Sanchez, B. Julián, P. Belleville, M. Popall, *J. Mater. Chem.* **2005**, *15*, 3559.

[3] C. J. Adams, A. Angeloni, A. G. Orpen, T. J. Podesta, B. Shore, *Cryst. Growth des.* **2006**, *6*, 411.

[4] B. Zhang, Y. Zhang, Z. Wang, D. Yang, Z. Gao, D. Wang, Y. Guo, D. Zhu, T. Mori, *Dalton Trans.* **2016**, *45*, 16561.

[5] N. Lashgari, A. Badiei, G. Mohammadi Ziarani, *Nanochem. Res.* **2016**, *1*, 127.

[6] S. Tao, Y. Chen, J. Cui, H. Zhou, N. Yu, X. Gao, S. Cui, C. Yuan, M. Liu, M. Wang, X. Wang, H. Gong, Y. Li, T. Liu, X. Sun, J. Yin, X. Zhang, M. Wu, *Chem. Commun.* **2020**, *56*, 1875.
[7] E. Santos, J. Albo, A. Irabien, *RSC Adv.* **2014**, *4*, 40008.
[8] L. Fu, H. Gao, M. Yan, S. Li, X. Li, Z. Dai, S. Liu, *Small* **2015**, *11*, 2938.
[9] J. Bäcker, S. Mihm, B. Mallick, M. Yang, G. Meyer, A.-V. Mudring, *Eur. J. Inorg. Chem.* **2011**, *2011*, 4089.
[10] M. D. Zidan, M. M. Al-Ktaifani, A. Allahham, *Optik* **2015**, *126*, 1491.
[11] P. Gogoi, A. K. Dutta, P. Sarma, R. Borah, *Appl. Catal. A. Gen.* **2015**, *492*, 133.
[12] A. Zare, M. Dianat, M. M. Eskandari, *New J. Chem.* **2020**, *44*, 4736.
[13] A. Khazaei, A. R. Moosavi-Zare, S. Firoozmand, M. R. Khodadadian, *Appl. Organomet. Chem.* **2018**, *32*, e4058.
[14] H. Dong, Q. Liu, Y. Tian, Y. Qiao, *J. Chem. Res.* **2018**, *42*, 463.
[15] M. Torabi, M. Yarie, M. A. Zolfigol, S. Azizian, *Res. Chem. Intermed.* **2020**, *46*, 891.
[16] A. K. Dutta, P. Gogoi, R. Borah, *Appl. Organomet. Chem.* **2018**, *32*, e3900.
[17] A. Saha, S. Payra, A. Asatkar, A. R. Patel, S. Banerjee, *Curr. Organocatal.* **2019**, *6*, 177.
[18] M. Rostami, A. Khosropour, V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, *Appl. Catal. A. Gen.* **2011**, *397*, 27.
[19] A. Zare, A. Kohzadian, Z. Abshirini, S. S. Sajadikhah, J. Phipps, M. Benamarad, M. H. Beyzavi, *New J. Chem.* **2019**, *43*, 2247.
[20] J. P. Wan, Y. F. Chai, J. M. Wu, Y. J. Pan, *Synlett* **2008**, *19*, 3068.
[21] M. Rodriguez, P. Dubreuil, J. P. Bali, J. Martinez, *J. Med. Chem.* **1987**, *30*, 758.
[22] M. Goodman, H. Shao, *Pure Appl. Chem.* **1996**, *68*, 1303.
[23] S. Panja, S. Ghosh, K. Ghosh, *New J. Chem.* **2018**, *42*, 6488.
[24] A. S. Tomcufcik, S. D. Willson, A. W. Vogel, *US Patent* **1963**, *3*, 085.
[25] S. Rayavarapu, S. K. Kadiri, M. B. Gajula, M. Nakka, R. Tadikonda, N. S. Yarla, S. Vidavalur, *Med. Chem.* **2014**, *4*, 367.
[26] E. Debroye, S. V. Eliseeva, S. Laurent, L. V. Elst, S. Petoud, R. N. Muller, T. N. Parac-Vogt, *Eur. J. Inorg. Chem.* **2013**, *2013*, 2629.
[27] K.-H. Jung, H.-K. Kim, J.-A. Park, K. S. Nam, G. H. Lee, Y. Chang, T.-J. Kim, *ACS Med. Chem. Lett.* **2012**, *3*, 1003.
[28] X. Wang, J. Zhao, M. Le, H. Lin, J. Luan, G. Liu, X. Wang, *J. Inorg. Organomet. Polym. Mater.* **2018**, *28*, 800.
[29] T. Niwa, U. Doi, T. Osawa, *J. Agric. Food Chem.* **2003**, *51*, 90.
[30] C. Zhou, J. Xu, *Curr. Org. Synth.* **2013**, *10*, 394.
[31] K. W. Henderson, W. J. Kerr, *Chem. A Eur. J.* **2001**, *7*, 3430.
[32] H. R. Saadati-Moshtaghin, *Res. Chem. Intermed.* **2019**, *45*, 3077.
[33] B. Maleki, F. Mohammadi Zonoz, H. A. Akhlaghi, *Org. Prep. Proced. Int.* **2015**, *47*, 361.
[34] M. Kour, S. Paul, *New J. Chem.* **2015**, *39*, 6338.
[35] G. Ramachandran, R. Saraswathi, M. Kumarraja, P. Govindaraj, T. Subramanian, *Synth. Commun.* **2018**, *48*, 216.
[36] H. R. Saadati-Moshtaghin, F. M. Zonoz, M. M. Amini, *J. Solid State Chem.* **2018**, *260*, 16.
[37] A. Zare, R. Khanivar, N. Irannejad-Gheshlaghchaei, M. H. Beyzavi, *ChemistrySelect* **2019**, *4*, 3953.
[38] T. L. Lambat, S. S. Deo, F. S. Inam, T. B. Deshmukh, A. R. Bhat, *Karbala Int. J. Mod. Sci.* **2016**, *2*, 63.
[39] B. Maleki, M. Baghayeri, *RSC Adv.* **2015**, *5*, 79746.
[40] A. Mouradzadegun, S. Elahi, F. Abadast, *RSC Adv.* **2014**, *4*, 31239.
[41] F. Tamaddon, H. Kargar-Shooroki, A. A. Jafari, *J. Mol. Catal. a: Chem.* **2013**, *368–369*, 66.
[42] S. Naeim-Fallahiyeh, E. Rostami, H. Golchaman, S. Kaman-Torki, *Res. Chem. Intermed.* **2020**, *46*, 4141.
[43] M. Himaja, D. Poppy, K. Asif, *Int. J. Res. Ayurveda Pharm.* **2011**, *2*, 1079.
[44] H. Dong, Q. Fan, G. Luo, T. Zhang, H. Yang, Q. Liu, G. Zhao, J. Yang, *ChemistrySelect* **2019**, *4*, 8338.
[45] T. Zhang, W. Zhang, H. Dong, Q. Liu, *J. Mex. Chem. Soc.* **2020**, *64*, in press. https://doi.org/10.29356/jmcs.v64i1.1034
[46] A. Zare, E. Sharif, A. Arghoon, M. Ghasemi, B. Dehghani, S. Ahmad-Zadeh, F. Zarei, *Iran. J. Catal.* **2017**, *7*, 233.
[47] N. Irannejad-Gheshlaghchaei, A. Zare, S. S. Sajadikhah, A. Banaei, *Res. Chem. Intermed.* **2018**, *44*, 6253.
[48] D. Wyrzykowski, T. Maniecki, A. Pattek-Janczyk, J. Stanek, Z. Warnke, *Thermochim. Acta* **2005**, *435*, 92.
[49] E. Styczeń, A. Pattek-Janczyk, M. Gazda, W. K. Jońwiak, D. Wyrzykowski, Z. Warnke, *Thermochim. Acta* **2008**, *480*, 30.
[50] A. Saha, S. Payra, D. Dutta, S. Banerjee, *ChemPlusChem* **2017**, *82*, 1129.
[51] A. Zare, T. Yousofi, A. R. Moosavi-Zare, *RSC Adv.* **2012**, *2*, 7988.
[52] H. Haji Andevary, A. Akbari, M. Omidkhah, *Fuel Process. Technol.* **2019**, *185*, 8.
[53] B. Mombani Godajdar, A. R. Kiasat, M. Mahmoodi Hashemi, *J. Mol. Liq.* **2013**, *183*, 14.
[54] H. Liu, R. Zhao, X. Song, F. Liu, S. Yu, S. Liu, X. Ge, *Catal. Lett.* **2017**, *147*, 2298.

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