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Application of Deep Eutectic Solvents with Dual Function as Reaction Medium and Catalyst for the Green Synthesis of Azoarene and Azoxyarene Derivatives

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Abstract
An environmentally friendly and safe method has been developed for synthesizing Azoarene and Azoxyarene derivatives from readily available nitrobenzene. This process utilizes a deep eutectic solvent (DES) composed of choline chloride (ChCl) and zinc chloride ($ZnCl_2$), which functions as both the catalyst and reaction medium. The methodology is leveraging the dual role of the ChCl/$ZnCl_2$ DES. Using this approach, various Azo and Azoxy compounds have been successfully synthesized starting from nitrobenzene derivatives. The reaction proceeded efficiently under mild conditions (3 h at 60 °C). Notably, the system exhibited strong selectivity toward Azoxy products, which were obtained in high yields of 73-78%. In contrast, Azo derivatives were formed only in moderate yield (42%), highlighting the selective nature of the ChCl/$ZnCl_2$ DES catalytic medium. This method not only simplifies the synthesis but also aligns with the principles of green chemistry, offering an efficient and sustainable approach to producing Azoarene and Azoxyarene derivatives.

Keywords
Deep eutectic solvents (DESs); ChCl/ZnCl2 catalytic system; Nitrobenzene reduction; Azoarene and Azoxyarene synthesis; Green chemistry; Selective reduction.

1. INTRODUCTION

Azo and Azoxy compounds are notable organic molecules in the dye and pigment industries due to their ability to produce bright, vibrant colors [1]. These compounds exhibit intense chromatic properties and can be tailored for various applications, such as textiles and inks [2]. Additionally, they have garnered significant attention from researchers in organic synthesis and pharmaceuticals due to their versatile reactivity [3], often serving as key intermediates in a range of chemical reactions [4]. Azo and Azoxy compounds are also frequently studied for their heat resistance [5] and their potential to act as ligands in coordination chemistry [6]. Given these attributes, extensive research has focused on their properties, applications, and potential advancements [7,8]. Since the synthesis of these compounds is crucial, several methods have been developed, including traditional oxidation and reduction techniques, the use of heavy metals, and electrochemical processes.

In oxidation and reduction processes, azo and azoxy compounds can be synthesized either by oxidizing amines or reducing nitro compounds [9-14]. For example, Singh et al. demonstrated that H_2O_2, when combined with gallium oxide nanorods and aluminum oxide as heterogeneous catalysts, serves as a powerful oxidizing agent for transforming aromatic amines into azoxy compounds [15]. Similarly, Yu et al. employed an I2/DABCO system to mediate the oxidative coupling of nitrosobenzenes with aromatic amines, resulting in the formation of unsymmetrical aromatic azoxy compounds [16]. In another study, Rezaeifard et al. utilized $Bu4NHSO_5$ in CH_3CN as a selective approach for synthesizing symmetrical Azoarenes [17]. Waghmode et al.

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used tertiary butyl hydroperoxide with ETS-10 as a catalyst to oxidize aryl amines into azoxybenzenes [18].

Some researchers have also focused on reduction methods. For instance, Liu et al. reported that aromatic nitro compounds can be efficiently transformed into their corresponding azo and azoxy compounds using 2-propanol as a reducing agent, with Au/meso-Ce_2 serving as an effective catalyst [19]. Additionally, Belattar et al. developed a catalytic method for the reduction of nitroarenes using NaBH4 and diphenyl diselenide as a catalyst, achieving Azoxyarenes and Azoarenes under mild conditions [20]. In this reaction, diphenyl diselenide is first transformed into sodium phenylselenolate, which acts as an electron-transfer agent, facilitating the reduction of various nitroarenes. Similarly, Di Gioia et al. used $LiAlH_4$ and TiO_2 to reduce nitrobenzene derivatives for this purpose [21].

Although traditional oxidants and reductants offer high yields, they often require toxic solvents [22], as well as expensive and complex catalysts that are difficult to separate from the reaction medium after completion [23]. These factors contribute to environmental pollution and increase greenhouse gas emissions [24,25]. Additionally, their safety and environmental impact are major concerns [26-31].

As previously mentioned, many researchers have explored the use of heavy metals [32-35] and electrochemical synthesis [36,37]. However, heavy metals pose significant drawbacks, including health risks to humans even at low concentrations [38]. Although electrochemical synthesis is considered a green method, it requires complex and expensive equipment [39], customized cells [40], and costly membranes [41].

In line with the principles of green chemistry, the adoption of biodegradable and non-toxic solvents is crucial for mitigating environmental pollution [42-44]. Deep eutectic solvents (DESs) have gained recognition in recent decades as potential alternatives to traditional organic solvents due to their non-flammability [45], low vapor pressure [46], thermal stability [47], and ability to function as both solvents and catalysts [48-51]. DESs share many properties with ionic liquids, and both are considered green solvents [52-54]. A key advantage of DESs lies in their excellent recyclability and ease of separation from the reaction mixture, allowing them to be recovered and reused without complex purification steps. While previous methods have employed easily separable heterogeneous catalysts, DESs offer an alternative that combines green solvent properties with catalytic activity in a sustainable manner. This makes DESs highly efficient and practical for sustainable and green chemistry applications [55]. Consequently, researchers have emphasized the benefits of DESs in their studies [56-58].As a result, we developed a conceptual approach in which deep eutectic solvents (DESs) can serve dual roles as both green solvents and catalysts, offering a sustainable alternative to traditional methods. Azo compounds are primarily applied in textile dyes and pigments due to their bright colors and colorfastness, whereas azoxy compounds are especially valuable in pharmaceuticals and as intermediates in organic synthesis because of their unique reactivity. Furthermore, it should be noted that the properties of DESs, such as biodegradability, toxicity, and recyclability, strongly depend on the choice of their hydrogen bond donors and acceptors. While previous methods have employed easily separable heterogeneous catalysts, DESs offer an environmentally friendly strategy that combines solvent and catalytic functions in a sustainable manner. Therefore, the aim of the present study is to develop a green, efficient, and high-yielding method for the synthesis of azo and azoxy compounds using DESs, highlighting their potential for sustainable organic synthesis.

2. EXPERIMENTAL

2.1. Materials and methods

All compounds used in this research including choline chloride (ChCl), zinc chloride ($ZnCl_2$), Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), tin(II) chloride dihydrate ($SnCl_2{\cdot}2H_2O$), nickel(II) chloride hexahydrate ($NiCl_2.6H_2O$), copper(II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$), acetic acid (AcOH), p-toluenesulfonic acid (pTSA), urea, ethylene glycol, sodium hydroxide (NaOH), n-hexane, ethyl acetate, and silica gel were commercially available and supplied by Hakim-Gostar Chemical Co. (Tehran, Iran), with products sourced from Sigma-Aldrich (St. Louis, MO, USA) and Merck (Darmstadt, Germany).

2.2. Instruments

A Buchi 535 melting point apparatus was used for the melting point measurements. ^{1}HNMR (400 MHz, $CDCl_3$) spectra were recorded on an Avance III 400 MHz spectrometer (Bruker, Germany), using tetramethylsilane (TMS) as the internal standard to reference chemical shifts.

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2.3. Preparation of deep eutectic solvents

The DES mixtures were prepared by combining choline chloride (ChCl) with various components, including $FeCl_3 \cdot 6H_2O$, $SnCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2 \cdot 2H_2O$, urea, ethylene glycol, p-toluenesulfonic acid (pTSA), and acetic acid (AcOH), following methods established in the literature [59,60]. The key DESs were prepared by combining choline chloride (ChCl) with various hydrogen bond donors (HBDs) in defined molar ratios, following established procedures [59,60]. The components were stirred and heated at 60 °C for 0.5 h until a homogeneous liquid was obtained. The exact compositions and molar ratios for each DES are summarized in Table 1.

2.4. Product monitoring and characterization

The progress of all reactions was carefully monitored using thin layer chromatography (TLC). A solvent mixture of n-hexane and ethyl acetate in a 3:1 ratio was employed to achieve optimal separation of the reactants and products. All synthesized products corresponded to previously reported compounds, and their identities were confirmed by comparing their melting points with literature values. This approach ensured the reliability and reproducibility of the synthetic procedures while providing a straightforward method for verifying product formation.

2.5. Procedure for synthesizing Azo and Azoxy derivatives

A mixture of ChCl:$ZnCl_2$ (0.05 mmol, corresponding to 15 mg), 4-chloro nitrobenzene (1 mmol), and NaOH (1.2 mmol) was placed in a 25 mL flask and stirred at 60 °C for 3 h (Fig. 1). The progress of the reaction was monitored by TLC, using a 3:1 n-hexane and ethyl acetate mixture as the eluent. After completion of the reaction, the mixture was cooled, and 50 mL of water and 50 mL of ethyl acetate were added to the flask. The ChCl dissolved in the aqueous phase, while the remaining components partitioned into the organic phase. The two phases were then separated, and the organic phase was dried over $MgSO_4$. The product was purified from the concentrated organic layer by silica gel chromatography on a glass plate, using a 10:1 n-hexane to ethyl acetate mixture as the mobile phase. The identity of the known products was confirmed through melting point determination and spectral analysis, including ^{1}HNMR. Full characterization data are provided, and the original spectra can be found in the Figs. 2-5. The FTIR spectra of the four synthesized azo-oxide derivatives were recorded and analyzed to confirm their structural features (Fig. 6). All spectra exhibit characteristic aromatic C–H stretching vibrations in the region of 3020–3050 cm^{-1}, indicating the presence of aromatic rings in each compound. Strong and distinctive carbonyl stretching bands appear for the bis(4-carboxyphenyl)diazene oxide derivative at 1710 and 1680 cm^{-1}, consistent with the presence of carboxylic acid functionalities. The azo N=N and N→O functionalities contribute to the bands observed in the 1600–1610 cm^{-1} region across all derivatives. Additional signals in the fingerprint region, including C–O, C–X (X = Br, Cl), and para-substituted aromatic C–H out-of-plane bending vibrations, further support the successful introduction of the corresponding substituents in each molecule. Notably, the bis(4-bromophenyl) and bis(4-chlorophenyl) derivatives display strong halogen-associated bands around 830–840 and 760–780 cm^{-1}, whereas the di-p-tolyl derivative exhibits characteristic methyl C–H bending at 1365 cm^{-1}. Overall, the FTIR analysis corroborates the successful synthesis of all four derivatives, confirming the presence of their key functional groups and providing evidence consistent with the structural assignments deduced from NMR data.

3. RESULTS AND DISCUSSION

Different deep eutectic solvents were tested for the synthesis of (Z)-1,2-bis(4-chlorophenyl)diazene oxide to optimize reaction conditions. 4-Chloronitrobenzene was selected as the model reactant, and the reaction was conducted on a gram scale to determine the optimal DES type, DES mixture, reaction temperature, and reaction time. As shown in Table 2, reaction 1 demonstrates that no product was formed in the absence of a catalyst. Therefore, various DESs were evaluated as reaction media (reactions 2-10) to identify the most effective solvent. The results indicate that ChCl/$ZnCl_2$ (entry 5) produced the highest yield. In addition, the reaction was tested in the presence of several non-metallic, neutral, or basic DESs, such as ChCl/EG, ChCl/pTSA, ChCl/Urea, and ChCl/AcOH (reactions 7-10), but these yielded significantly lower product amounts.

To investigate the role of ChCl, a strong acid and a quaternary ammonium salt were tested: pTSA/$ZnCl_2$ and TBAB/$ZnCl_2$ (reactions 11-12). Additionally, the reaction was conducted in H_2 O, a traditional green solvent, for comparison (reaction 13), but no significant yield was obtained. Next, each component of the most effective DES (ChCl/$ZnCl_2$) was tested individually to determine their contributions to the reaction. Using ChCl alone yielded no product (reaction 14), while $ZnCl_2$ alone resulted in a 35% yield (reactions 15). These findings highlight the

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necessity of both components to achieve optimal reaction conditions.

Table 1. Composition, molar ratios, and masses of key DESs.

DES No.	HBS (ChCl)	HBD	Molar Ratio (ChCl:HBD)	Mass of ChCl (g)	Mass of HBD (g)
1	ChCl	$ZnCl_2.2H_2O$	1:2	0.28	0.69
2	ChCl	$FeCl_3.6H_2O$	1:1	0.28	0.20
3	ChCl	$SnCl_2.2H_2O$	1:1	0.28	0.22
4	ChCl	$NiCl_2.6H_2O$	1:1	0.28	0.33
5	ChCl	$CuCl_2.2H_2O$	1:1	0.28	0.28
6	ChCl	Urea	1:2	0.28	0.17
7	ChCl	Ethylene glycol	1:2	0.28	0.17
8	ChCl	p-Toluenesulfonic acid (pTSA)	1:1	0.28	0.38
9	ChCl	Acetic acid (AcOH)	1:1	0.28	0.16

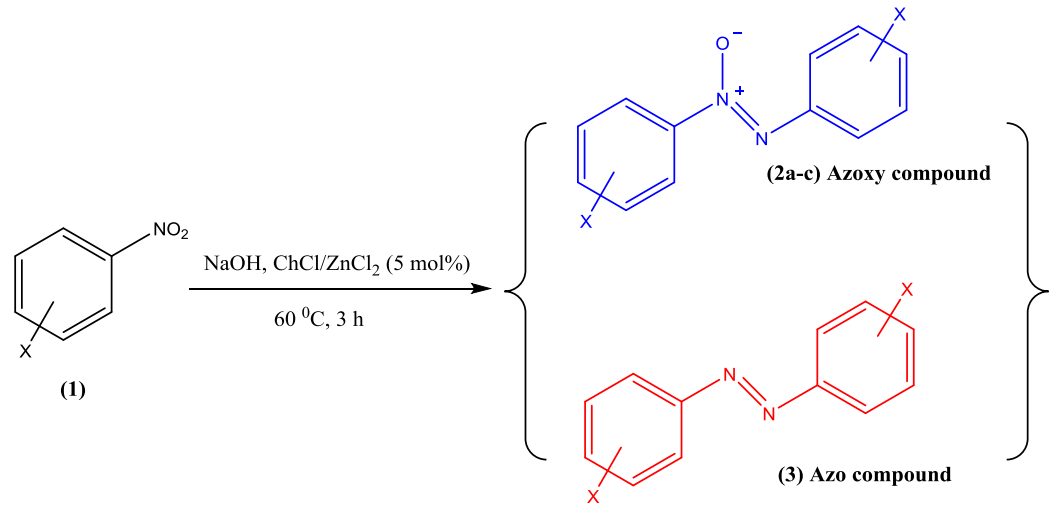

Fig. 1. Schematic representation of the synthesis of Azo and Azoxy derivatives.

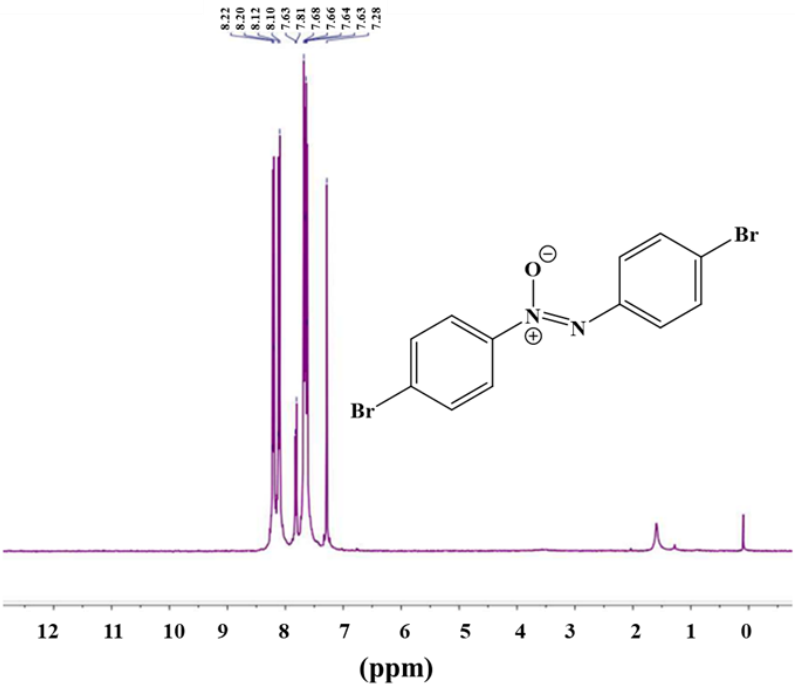

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Fig. 2. The 1HNMR of (Z)-1,2-bis(4-bromophenyl)diazene oxide, (C12H8Br2N2O). Yield: 78%; 1HNMR (400 MHz, CDCl3) δ: 8.21 (d, J = 9.1 Hz, 2H), 8.11 (d, J = 9.0 Hz, 2H), 7.67 (d, J = 9.2 Hz, 2H), 7.63 (d, J = 9.1 Hz, 2H), m.p.: 163°C, Shimmering yellow flakes.

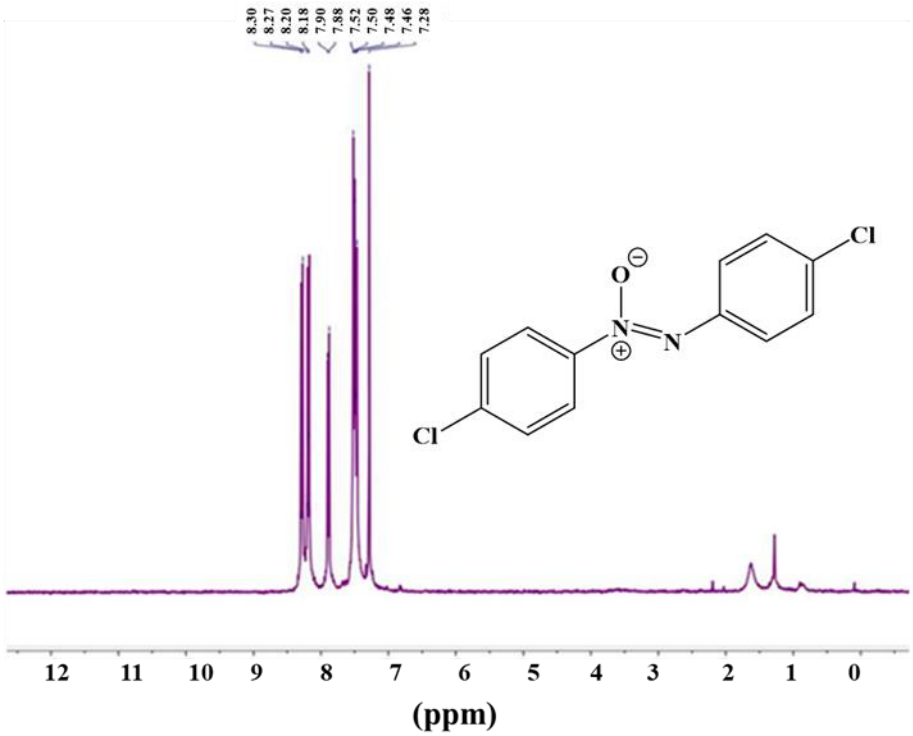

Fig. 3. The 1HNMR of (Z)-1,2-bis(4-chlorophenyl)diazene oxide (C12H8Cl2N2O). Yield: 75%; 1HNMR (400 MHz, CDCl3) δ: 8.28 (d, J = 9.1 Hz, 2H), 8.19 (d, J = 9.0 Hz, 2H), 7.51 (d, J = 9.1 Hz, 2H), 7.47 (d, J = 9.0 Hz, 2H). m.p: 147 °C, pale yellow solid.

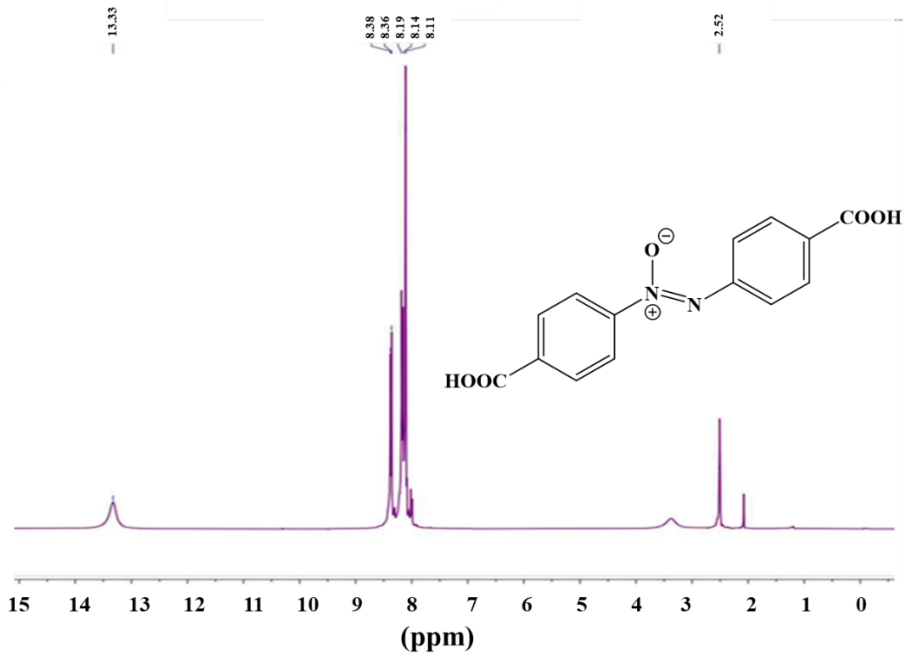

Fig. 4. The 1HNMR of (Z)-1,2-bis(4-carboxyphenyl)diazene oxide (C14H10N2O5). Yield: 73%; 1HNMR (400 MHz, CDCl3), δ (ppm), J (Hz): 8.11-8.19 (m, 6H), 8.37 (d, 2H, H2, J = 8.4 Hz), 13.33 (s, 2H, CO2H), m.p.: > 300.0 °C, dark yellow flakes.

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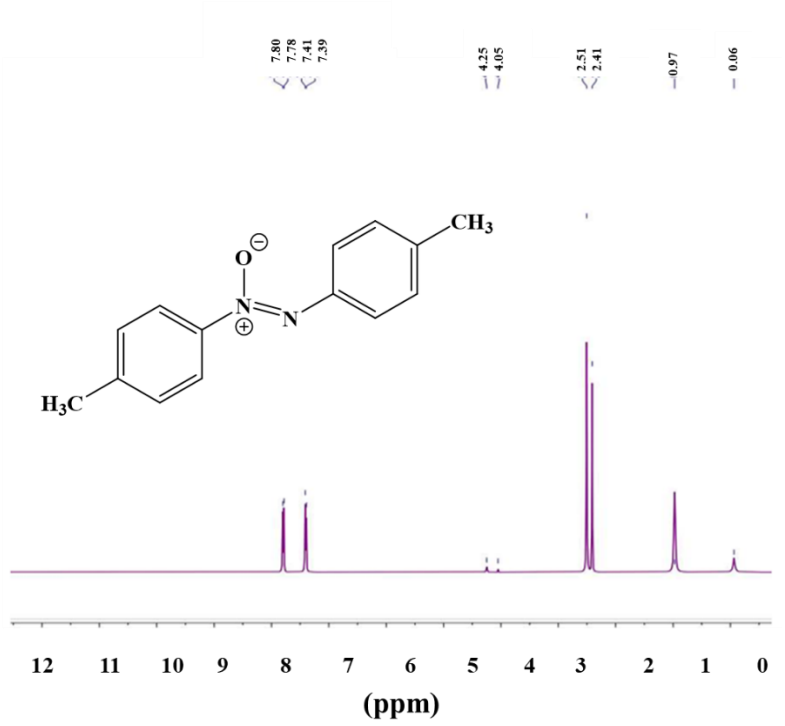

Fig. 5. The 1HNMR of (Z)-1,2-di-p-tolyldiazene oxide (C14H14N2). Yield: 42%, 1HNMR (400 MHz, CDCl3) δ: 7.79 (d, J = 7.87 Hz, 4H), 7.4 (d, J = 7.84 Hz, 4H), 2.41 (s, 6H), m.p.: 146 °C; yellow solid.

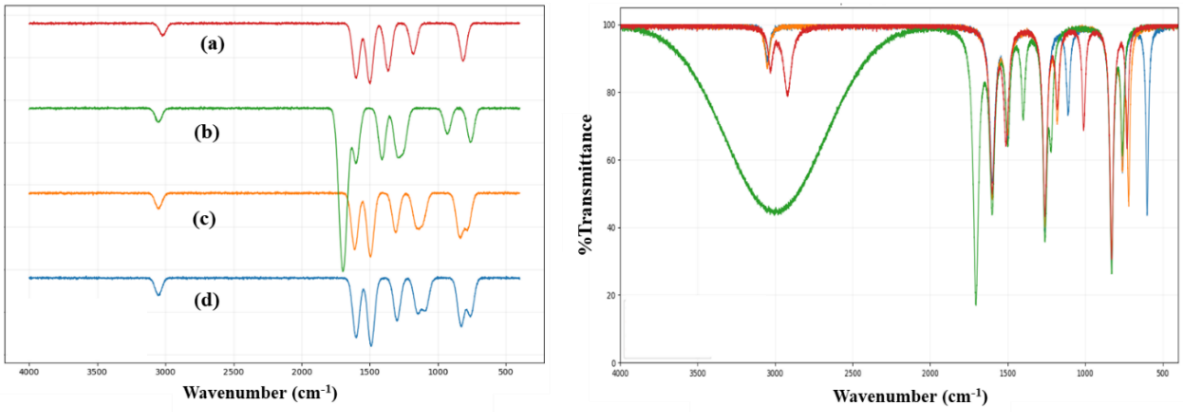

Fig. 6. FTIR of (a) (Z)-1,2-bis(4-bromophenyl)diazene oxide, (b) (Z)-1,2-bis(4-chlorophenyl)diazene oxide, (c) (Z)-1,2-bis(4-carboxyphenyl)diazene oxide, (d) (Z)-1,2-di-p-tolyldiazene oxide.

In the next phase of optimization, reaction temperatures were varied at 40 °C, 80 °C, and 100 °C (reactions 16-18), compared to the initial 60 °C used in reaction 5. Increasing the temperature to 80 °C or 100 °C resulted in a slight decrease in yield, while reducing the temperature to 40 °C significantly lowered both the reaction rate and product yield. Thus, 60 °C was confirmed as the optimal temperature. Subsequently, the reaction time was optimized (reactions 19-22).

Initially, the time was extended to 15 h (reaction 19) under the same conditions as reaction 5, but this did not improve the yield. Consequently, 3 h was determined to be the optimal duration for this reaction, as confirmed by TLC monitoring, which showed no considerable further progress beyond this period.

Finally, the effect of DES concentration was examined by testing 2.5, 7.5, and 10 mol% catalyst (reactions 23-25). Increasing the catalyst concentration from 2.5 to 5 mol% improved the reaction efficiency. However, increasing the concentration to 7.5 or 10 mol% did not significantly affect the yield. Therefore, 5 mol% catalyst (reaction 5) was deemed sufficient for this reaction.

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Table 2. The outcomes of optimal condition of the reaction.

Reaction (entry)	medium	mol/(%) (g)	Temp./(°C)	Duration/ (h)	Yield/(%)
1	-	-	60	10	NR
2	ChCl/ $(CuCl_2)_2$	5 (0.028)	60	10	60
3	ChCl/$(FeCl_3)_2$	5 (0.024)	60	10	71
4	ChCl/$(SnCl_2)_2$	5 (0.025)	60	10	30
5	ChCl/$(ZnCl_2)_2$	5 (0.049)	60	10	79
6	ChCl/$(NiCl_2)_2$	5 (0.031)	60	10	57
7	ChCl/$(EG)_2$	5 (0.023)	60	10	Fade
8	ChCl/$(pTSA)_2$	5 (0.033)	60	10	36
9	ChCl/$(Urea)_2$	5 (0.023)	60	10	Fade
10	ChCl/$(AcOH)_2$	5 (0.022)	60	10	41
11	pTSA/$ZnCl_2$	5 (0.054)	60	10	38
12	TBAB/$ZnCl_2$	5 (0.062)	60	10	34
13	H_2O	-	60	10	40
14	ChCl	5 (0.014)	60	10	NR
15	$ZnCl_2$	5 (0.035)	60	10	35
16	ChCl/$(ZnCl_2)_2$	5 (0.049)	40	10	29
17	ChCl/$(ZnCl_2)_2$	5 (0.049)	80	10	72
18	ChCl/$(ZnCl_2)_2$	5 (0.049)	100	10	67
19	ChCl/$(ZnCl_2)_2$	5 (0.049)	60	15	80
20	ChCl/$(ZnCl_2)_2$	5 (0.049)	60	5	77
21	ChCl/$(ZnCl_2)_2$	5 (0.049)	60	3	75
22	ChCl/$(ZnCl_2)_2$	5 (0.049)	60	1	32
23	ChCl/$(ZnCl_2)_2$	2.5 (0.024)	60	3	42
24	ChCl/$(ZnCl_2)_2$	7.5 (0.073)	60	3	77
25	ChCl/$(ZnCl_2)_2$	10 (0.097)	60	3	78

Based on the optimization results, the best reaction conditions were obtained using ChCl/$ZnCl_2$ as the reaction medium. The catalytic effect of Zn^{2+} played a crucial role in promoting the formation of azoxy linkages, outperforming other metal chlorides such as $FeCl_3$ and $CuCl_2$. A concentration of 5 mol% $ZnCl_2$ was found to be optimal, as increasing the concentration to 7.5 % or 10 % did not significantly enhance the yield. The optimal temperature was determined to be 60°C, as higher temperatures (80 °C and 100 °C) led to lower yields, possibly due to side reactions or decomposition. The reaction time of 3 h was optimal, yielding 75 %, with no significant improvement for longer durations. Notably, in the absence of a catalyst, the reaction did not proceed, and alternative catalysts such as pTSA/$ZnCl_2$ and TBAB/$ZnCl_2$ resulted in lower yields, further highlighting the critical role of $ZnCl_2$ in this system.

A plausible mechanistic hypothesis for the catalytic role of the ChCl/ZnCl2 DES involves the activation of the nitro or amine groups by Zn2+ coordination, which increases their electrophilicity and facilitates the formation of azoxy linkages (Fig. 7). Meanwhile, the choline chloride component may stabilize reaction intermediates through hydrogen bonding networks, promoting the selective formation of the desired products. This synergistic interaction between Zn^{2+} and ChCl provides an efficient catalytic environment, explaining the superior yields observed with this DES compared to other tested solvents or DES mixtures. Control experiments were systematically performed using each individual component of the DES, alternative DES mixtures, and conventional green solvents. These experiments confirmed that both choline chloride and $ZnCl_2$ are essential for efficient formation of azoxy linkages, while reactions with only one component or with other DESs resulted in significantly lower yields. Moreover, the control studies highlighted the limitations of alternative catalysts and solvents, demonstrating that many conventional or neutral DESs fail to promote the reaction effectively, thereby underscoring the unique synergistic effect of the chosen DES system. After optimizing the reaction conditions, a literature review identified three studies that employed a similar approach for the synthesis of azoxy compounds [61-63]. To highlight the effectiveness of the current green method, a comparison with these previous studies is presented in Table 3. In these studies, the starting materials included 1-bromo-4-nitrobenzene, 1-chloro-4-nitrobenzene, 4-nitrobenzoic acid, and 1-methyl-4-nitrobenzene. In our substrate scope study, the synthesized azoarene derivatives were obtained in yields of 73-78%, while the azoxy derivative was achieved in 42%. These yields represent the results obtained in the present work.

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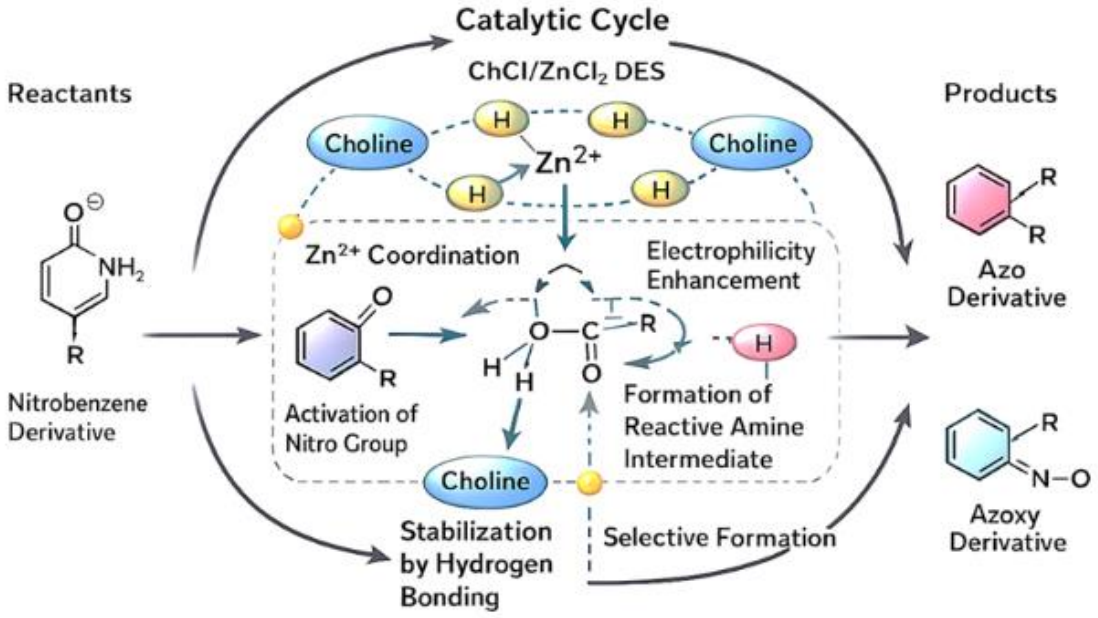

Fig. 7. Proposed mechanistic hypothesis for the catalytic function of $ChCl/ZnCl_2$ DES in the synthesis of Azo and Azoxy derivatives.

Among the various methods for synthesizing Azoxyarenes from nitrobenzene derivatives, the present method offers several distinct advantages. Notably, it reduces the reaction time to just 3 h, compared to 1, 2–6, and 5 h reported in previous studies. Furthermore, this method employs a deep eutectic solvent (DES) as both the reaction medium and catalyst providing a green and and recyclable alternative to conventional solvents, a key advantage over previous methods, which contributes to improved safety by minimizing the risks associated with flammability, toxicity, and environmental impact. The DES acts as a recyclable reaction medium and catalyst. Its low vapor pressure and ease of recovery offer practical advantages over conventional solvents.

Table 3. Comparison of $ChCl/ZnCl_2$ with previous studies on the synthesis of azo, and azoxy compounds.

Catalyst	Conditions	Duration/ (h)	Amount	Yield/ (%)	Ref.
PEG 400	Reflux, Benzene	1	8 mmol	80	[61]
$BaTi_{1-x}Fe_xO_3$ (X=0 to 0.3)	Reflux, Isopropanol	2-6	BaTi (0.975 mg) Fe (0.025 mg), O_3	93	[62]
Au/P25	Argon gas, visible light, 40 °C, Isopropanol	5	100 mg	76	[63]
$ChCl:ZnCl_2$	60 °C	3	5 mol%	73-78	Current work

4. CONCLUSIONS

In summary, one azo and three azoxy derivatives were synthesized using a deep eutectic solvent (DES), which functioned as both the reaction medium and the catalytic component of the system. The $ChCl/ZnCl_2$ DES enabled the transformation of readily available nitrobenzene derivatives while reducing the need for conventional volatile organic solvents and additional catalytic reagents. The method benefits from the use of an inexpensive and easily accessible DES mixture, along with operationally simple reaction conditions. Although chromatographic purification was applied as part of the work-up—consistent with standard practice—the use of DES facilitated product isolation by allowing straightforward phase separation prior to purification. The protocol afforded consistently high yields, particularly for the azoxy derivatives, demonstrating the efficiency of this DES-based system for these transformations. Overall, this study provides a practical and resource-efficient approach for the synthesis of azo and azoxy compounds, supported by clear experimental outcomes and high product yields.

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Declaration of interest

The author declares no competing interests.

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REFERENCES

[1] K.Y. Cai, and Y.M. Zhou, Reduction of aromatic nitro compounds to azoxy compounds with sodium borohydride. *Adv. Mater. Res.* 1033 (2014) 18-21.

[2]S. Benkhaya, S. Mrabet, A. and Elharfi, Classifications, properties, recent synthesis and applications of azo dyes. *Heliyon* 6 (2020) e03271.

[3]B.G. Cai, C. Empel, W.Z. Yao, R.M. Koenigs, and J. Xuan, Azoxy compounds—from synthesis to reagents for azoxy group transfer reactions. *Angew. Chem.* 135 (2023) e202312031.

[4]H. Tan, X, Liu, J. Su, Y. Wang, X. Gu, D. Yang, E.R. Waclawik, H. Zhu, and Z. Zheng, One-pot selective synthesis of azoxy compounds and imines via the photoredox reaction of nitroaromatic compounds and amines in water. *Sci. Rep*. 9 (2019) 1280.

[5]V. Sinditskii, A. Burzhava, and A. Sheremetev, Macrocyclic tetra (azo-) and tetra (azoxyfurazan) s: Comparative study of decomposition and combustion with linear analogs. *Energ. Mater. Front.* 2 (2021) 87-95.

[6]M. Diab, A. El-Bindary, A. El-Sonbati, and O. Salem, Supramolecular structure and substituents effect on the spectral studies of oxovanadium (IV) azodyes complexes. *J. Mol. Struct.* 1018 (2012) 176-184.

[7]B.T. Newbold, Oxidation and synthetic uses of hydrazo, azo and azoxy compounds. *Hydrazo*, 1 (1975) 541-597.

[8]A. Patel, and T. Rosenau T, Synthesis and analytical characterization of all N–N-coupled, dimeric oxidation products of α-tocopheramine: hydrazo-, azo-, and azoxy-tocopherol. *Monatsh. Chem.* 152 (2021) 1231-1239.

[9]A. Shukla, R.K. Singha, T. Sasaki, S. Adak, S. Bhandari, V. Prasad, A. Bordoloi, and R. Bal, Room temperature selective reduction of nitroarenes to azoxy compounds over Ni-TiO_2 catalyst. *Mol. Catal.* 490 (2020)110943.

[10]F. Ferlin, M. Cappelletti, R. Vivani, M. Pica, O. Piermatti, and L. Vaccaro, Au@zirconium-phosphonate nanoparticles as an effective catalytic system for the chemoselective and switchable reduction of nitroarenes. *Green Chem.* 21 (2019) 614-626.

[11]X. Chong, C. Liu, Y. Huang, C. Huang, and B. Zhang, Potential-tuned selective electrosynthesis of azoxy-, azo-and amino-aromatics over a CoP nanosheet cathode. *Natl. Sci. Rev.* 7 (2020) 285-295. ‘

[12]Z. Yan, X. Xie, Q. Song, F. Ma, X. Sui, Z. Huo, and M. Ma, Tandem selective reduction of nitroarenes catalyzed by palladium nanoclusters. *Green Chem.* 22 (2020) 1301-1307.

[13]X. Dai, Q. Wei, T. Duong, and Y. Sun, Selective transfer coupling of nitrobenzene to azoxybenzene on rh nanoparticle catalyst promoted by photoexcited hot electrons. *Chem. Nano Mat.* 5 (2019) 1000-1007.

[14]M.N. Pahalagedara, L.R. Pahalagedara, J. He, R. Miao, B. Gottlieb, D. Rathnayake, and S.L. Suib, Room temperature selective reduction of nitrobenzene to azoxybenzene over magnetically separable urchin-like Ni/Graphene nanocomposites. *J. Catal.* 336 (2016) 41-48.

[15]B. Singh, D. Mandelli, and P.P. Pescarmona, Efficient and selective oxidation of aromatic amines to azoxy derivatives over aluminium and gallium oxide catalysts with nanorod morphology. *Chem. Cat. Chem.* 12 (2020) 593-601.

[16]X. Yu, W. Ding, P. Ge, S. Wang, and J. Wang, Oxidative coupling of aromatic amines and nitrosoarenes: Iodine- mediated formation of unsymmetrical aromatic azoxy compounds. *Adv. Synth. Catal.* 360 (2016) 3150-3156.

[17]A. Rezaeifard, M. Jafarpour, S. Rayati, and R. Shariati, The catalytic performance of Mn-tetraarylporphyrins in the highly selective oxidation of primary aromatic amines to azo compounds by Bu_4NHSO_5. *Dyes Pigm.* 80 (2009) 80-85.

[18]S.B. Waghmode, S.M. Sabne, and S. Sivasanker, Liquid phase oxidation of amines to azoxy compounds over ETS-10 molecular sieves. *Green Chem.* 3 (2001) 285-288.

[19]X. Liu, S. Ye, H.Q. Li, Y.M. Liu, Y. Cao, and K.N. Fan KN, Mild, selective and switchable transfer reduction of nitroarenes catalyzed by supported gold nanoparticles. *Catal Sci. Technol.* 3 (2013) 3200-3206.

[20]N. Belattar, S. Benayache, and F. Benayache, Diphenyl diselenide–catalyzed reductive coupling of nitroarenes to aromatic azo and azoxy compounds with sodium borohydride in alkaline ethanol. *Curr. Org. Synth.* 15 (2018) 1182-1190.

[21]M.L. Di Gioia, A. Leggio, I.F. Guarino, V. Leotta, E. Romio, and A. Liguori, A simple synthesis of anilines by $LiAlH_4/TiCl_4$ reduction of aromatic nitro compounds. *Tetrahedron lett.* 56 (2015) 5341-5344.

[22]T. Welton, Solvents and sustainable chemistry. *Proc. R. Soc. A* 471 (2015) 20150502.

[23]A. Hussain, I. Ghafari, S. Sattar, M. Muneeb, A. Hasan, and B. Deepanraj, Eco-friendly catalysts revolutionizing energy and environmental applications: An overview. *Top. Catal.* 68 (2024) 487-509.

[24]A. Jiang, J. Li, K.J. Shah, and Z. You Z, Perspective Chapter: Implementing green chemistry principles for pollution control to achieve environmental sustainability–A Review. Green Chemi. Environ. Sustain. Prev. Assur. Sustain. *Approach* (2023).

[25]C. Chen, Y. Zhou, H. Fang, X. Peng, and L. Jiang, Progress and challenges in energy storage and utilization via ammonia. *Surf. Sci. Technol.* 1 (2023) 13.

[26]M. Miceli, P. Frontera, A. Macario, and A. Malara, Recovery/reuse of heterogeneous supported spent catalysts. *Catalysts* 11 (2021) 591.

[27]M. Panahimehr, S. Asghari, M. Hosseini, A. Mojaddami, Pd/$ZnMn_2O_4$ /chitosan nanobiocatalyst: A sustainable solution for sunlight-enhanced photocatalytic degradation of Congo red dye. *J. Mol. Struct.* 1347 (2025) 143339.

[28]M.M. Sadughi, M. Hosseini, and Karem Gallardo, Next-generation nanophotocatalyst for ultra-efficient and sustainable azithromycin decontamination: A breakthrough strategy for visible-light-driven pharmaceutical waste treatment. *Top. Catal.* (2025).

[29]M. Panahimehr, M. Hosseini, A. Mojaddami, and S. Karamipour, Eco-friendly synthesis of magnetic Pd/NiFe2O4/chitosan nanobiocatalyst for enhanced degradation of Congo red dye under sunlight irradiation. *Results Chem.* 15 (2025) 102300.

[30]M. Hosseini, Visible-light-assisted decontamination of sertraline in water using a Co3O4/g-C3N4 nanocomposite photocatalyst. *Environ. Sci. Pollut. Res.* 32 (2025) 20441-20460.

[31]M. Hosseini, M. Panahimehr, and S.M. Khoshfetrat, Solar-driven clopidogrel degradation with europium-enhanced ZnO nanocatalyst. *Int. J. Environ. Sci. Technol.* 22 (2025) 9915-9932.

[32]Z.P. Zhang, X.Y. Wang, K. Yuan, W. Zhu, T. Zhang, Y.H. Wang, J. Ke, X.Y. Zheng, C.H. Yan, and Y.W. Zhang, Free-standing iridium and rhodium-based hierarchically-coiled ultrathin nanosheets for highly selective reduction of nitrobenzene to azoxybenzene under ambient conditions. *Nanoscale* 8 (2016) 15744-15752.

[33]Z. Chen, Y. Qiu, X. Wu, Y. Ni, L. Shen, J. Wu, and S. Jiang, Highly selective reduction of nitrobenzenes to azoxybenzenes with a copper catalyst. *Tetrahedron Lett.* 59 (2018)1382-1384.

[34]J. Wang, X. Yu, C. Shi, D. Lin, J. Li, H. Jin, X. Chen, and S. Wang, Iron and nitrogen Co- doped mesoporous carbon- based heterogeneous catalysts for selective reduction of nitroarenes. *Adv. Synth. Catal.* 361 (2019) 3525-3531.

[35]Z. Hou, Y. Fujiwara, and H. Taniguchi, Lanthanides in organic synthesis. Samarium metal promoted selective formation of azoxy compounds. *J. Org. Chem.* 53 (1988) 3118-3120.

[36]D.S. Silvester, A.J. Wain, L. Aldous, C. Hardacre, and R.G. Compton, Electrochemical reduction of nitrobenzene and 4-nitrophenol in the room temperature ionic liquid [C_4dmim][$(NTf)_2$]. *J. Electroanal. Chem.* 596 (2006) 131-140.

[37]T. Wirtanen, E. Rodrigo, and S.R. Waldvogel, Recent advances in the electrochemical reduction of substrates involving N−O bonds. *Adv. Synth. Catal.* 362 (2020) 2088-2101.

[38]A.T. Jan, M. Azam, K. Siddiqui, A. Ali, I. Choi, and Q.M.R. Haq, Heavy metals and human health: mechanistic insight into toxicity and counter defense system of antioxidants. *Int. J. Mol. Sci.* 16 (2015) 29592-29630.

[39]C. Schotten, T.P. Nichollas, R.A. Bourne, N. Kapur, B.N. Nguyen, and C.E. Willans, Making electrochemistry easily accessible to the synthetic chemist. *Green Chem.* 22 (2020) 3358-3375.

[40]M. Webling, and H.J. Schafer, Cathodic hydrodimerization of nitroolefins. Beilstein *J. Org. Chem.* 11 (2015) 1163-1174.

[41]J.H. Jiang, B.L. Wu, and C.S. Cha, Electrosynthesis of p-methoxybenzaldehyde on graphite/Nafion membrane composite electrodes. *Electrochim. Acta* 43 (1998) 2549-2552.

[42]S.I. Kaya, A. Cetinkaya, and S.A. Ozkan, Green analytical chemistry approaches on environmental analysis. *Trends Environ. Anal. Chem.* 33 (2022) e00157.

[43]N. Behera, and A. Mishra, Green chemistry and catalysis: Current challenges and future perspectives. Encyclopedia of green materials. Springer, Singapore (2023).

[44]R. Ratti, Industrial applications of green chemistry: Status, Challenges and Prospects. *SN Appl. Sci.* 2 (2020) 263.

[45]M.S. Alvarez, M.A. Llongo, A. RodrigUuez, F.J. Deive, The role of deep eutectic solvents in catalysis. A vision on their contribution to homogeneous, heterogeneous and electrocatalytic processes. *J. Ind. Eng. Chem.* 132 (2024) 36-49.

[46]S.Khandelwal, Y.K. Tailor, and M. Kumar, Deep eutectic solvents (DESs) as eco-friendly and sustainable solvent/catalyst systems in organic transformations. *J. Mol. Liq.* 215 (2016) 345-386.

[47]R. Svigelj, N. Dossi, C. Grazioli, and R. Toniolo, Deep eutectic solvents (DESs) and their application in biosensor development. *Sensors* 21 (2021) 4263.

[48]S.E. Hooshmand, S. Kumar, I. Bahadur, T. Singh, and R.S. Varma, Deep eutectic solvents as reusable catalysts and promoter for the greener syntheses of small molecules: Recent advances. *J. Mol. Liq.* 371 (2023) 121013.

[49]A.E. Ünlu, A. Arikaya, and S Takac, Use of deep eutectic solvents as catalyst: A mini-review. *Green Process Synth.* 8 (2019) 355-372.

[50]S.P. Ijardar, V. Singh, and R.L. Gardas, Revisiting the physicochemical properties and applications of deep eutectic solvents. *Molecules* 27 (2022) 1368.

[51]Y. El-Baraka, G. Hamdoun, N. El-Brahmi, and S. El-Kazzouli, Unlocking the potential of deep eutectic solvents for C-H activation and cross-coupling reactions: A review. *Molecules* 28 (2023) 4651.

[52]M. Hosseini, Application of a new synthesized ionic liquid based on pyrrolidinium for microextraction of trace amounts of Cr (VI) ions in real water and wastewater samples. *J. Water Chem. Technol.* 45 (2023) 256-269.

[53]M. Hosseini, S.M. Khoshfetrat, M. Panahimehr, and A. Rezaei, ISFME extraction of As species from some real water samples using an imidazolium-based task-specific ionic liquid (TSIL): Synthesis and characterization. *Sep. Sci. Technol.* 59 (2024) 580-591.

[54]M. Hosseini, and K. Gallardo, A novel system based on a task-specific pyrrolinium-based ionic liquid and homogeneous in situ solvent formation microextraction for the determination of sertraline in real water and urine samples. *New J. Chem.* 49 (2025) 13772.

DOI: 10.30473/IJAC.2025.76239.1328

[55]J.K.U. Ling, and K. Hadinoto, Deep eutectic solvent as green solvent in extraction of biological macromolecules: A review. *Int. J. Mol. Sci.* 23 (2022) 3381.

[56]E.L. Smith, A.P. Abbott, and K.S. Ryder, Deep eutectic solvents (DESs) and their applications. *Chem. Rev.* 114 (2014)11060-11082.

[57]A. Prabhune, and R. Dey, Green and sustainable solvents of the future: Deep eutectic solvents. *J. Mol. Liq.* 379: (2023) 121676.

[58]J. Wang, S. Zhang, Z. Ma, and L. Yan, Deep eutectic solvents eutectogels: progress and challenges. *Green Chem. Eng.* 2 (2021) 359-367.

[59]B.S. Chalaki, N. Azizi, Z. Mirjafary, and H. Saeidian, Green and rapid oxidation of aldehydes using a catalyticapplications of deep uutectic solvent. *J. Saudi. Chem. Soc.* 28 (2024) 101915.

[60]S. Mandal, R. Narvariya, S.L. Sunar, I. Paul, A. Jain, and T.K. Panda, Synthesis of α-aminophosphorous derivatives using a deep eutectic solvent (DES) in a dual role. *Green Chem.* 25 (2023) 8266-8272.

[61]L. Liu, P. Concepcion, and A. Corma, Modulating the catalytic behavior of non-noble metal nanoparticles by inter-particle interaction for chemoselective hydrogenation of nitroarenes into corresponding azoxy or azo compounds. *J. Catal.* 369 (2019) 312-323.

[62]C. Srilakshmi, H. Vijay-Kumar, K. Praveena, C. Shivakumara, and M. Muralidhar Nayyak, A highly efficient iron doped $BaTiO_3$ nanocatalyst for the catalytic reduction of nitrobenzene to azoxybenzene. *RSC Adv.* 4 (2014) 18881-18884.

[63]Z. Zheng, J. Zhao, H. Liu, J. Liu, A. Bo, and H. Zhu, Painting anatase (TiO2) nanocrystals on long nanofibers to prepare photocatalysts with large active surface for dye degradation and prganic synthesis. *Chem. Cat. Chem.* 5 (2013) 2382-2388.

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بکارگیری حلال‌های یوتکتیک عمیق با عملکرد دوگانه به عنوان محیط و کاتالیزور برای سنتز سبز مشتقات آزوآرن و آزوکسی‌آرن

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چکیده

یک روش سازگار با محیط‌زیست و ایمن برای سنتز مشتقات آزوآرن و آزوکسی‌آرن از نیتروبنزن‌های در دسترس به‌طور گسترده توسعه یافته است. در این فرآیند از یک حلال یوتکتیک عمیق (DES) متشکل از کولین کلرید (ChCl) و روی کلراید ($ZnCl_2$) استفاده شده است که هم به‌عنوان کاتالیزور و هم به‌عنوان محیط واکنش عمل می‌کند. این روش با بهره‌گیری از نقش دوگانه DES $ChCl/ZnCl_2$، امکان سنتز موفقیت‌آمیز ترکیبات مختلف آزو و آزوکس را از مشتقات نیتروبنزن فراهم می‌آورد. واکنش تحت شرایط ملایم (۳ ساعت در ۶۰ درجه سانتی‌گراد) به‌طور کارآمد پیش رفت. شایان ذکر است که این سیستم انتخاب‌پذیری بالایی نسبت به محصولات آزوکس نشان داد، به‌طوری که این ترکیبات با بازده بالای ۷۳-۷۸٪ به‌دست آمدند. در مقابل، مشتقات آزو تنها با بازده متوسط (۴۲٪) تشکیل شدند که نشان‌دهنده ماهیت انتخابی محیط کاتالیزوری DES $ChCl/ZnCl_2$ است. این روش نه تنها سنتز را ساده می‌کند، بلکه با اصول شیمی سبز نیز همسو است و رویکردی کارآمد و پایدار برای تولید مشتقات آزوآرن و آزوکس‌آرن ارائه می‌دهد.

کلید واژه ها

حلال‌های یوتکتیک عمیق (DES)، سیستم کاتالیزوری $ChCl/ZnCl_2$، کاهش نیتروبنزن، سنتز آزوآرن و آزوکس‌آرن، شیمی سبز، انتخاب‌پذیری.

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