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Regioselective oxidative bromination of arenes by a metal–organic framework-confined mono-bipyridyl iron(III) catalyst†

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Oxidative bromination of arenes is an effective and environmentally friendly method for synthesizing bromoarenes. We have developed a highly robust zirconium metal–organic framework (MOF)-supported mono-bipyridyl iron(III) chloride catalyst (bpy–UiO–FeCl₃) for oxidative bromination of arenes using H₂O₂ as the oxidant and KBr as the bromine source. The bpy–UiO–FeCl₃ catalyst exhibits high conversion rates for various substituted arenes, yielding significant amounts of bromoarenes with excellent regioselectivity and recyclability under mild reaction conditions. The MOF catalyst outperforms its homogeneous counterparts in terms of both activity and regioselectivity due to the stabilization of the mononuclear bipyridyl–iron(III) species within the active sites within the MOF pores. Furthermore, the confinement of these active sites within the robust, well-defined, and uniform porous framework enhances the regioselectivity of bromination through shape-selective catalysis. The mechanism of bpy–UiO–FeCl₃-catalyzed oxidative bromination of arenes was thoroughly investigated by a combination of control experiments, spectroscopic analyses, and computational studies. These findings underscore the importance of MOFs in the development of heterogeneous catalysts based on Earth-abundant metals for the sustainable synthesis of haloarenes.

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Introduction

Halogenation reactions have gained significant importance as organohalides are essential chemicals with significant efficacy in pharmaceutical sciences,¹ materials sciences,² imaging techniques,³ and organic synthesis.^{4–6} Bromoarenes, in particular, are important synthetic precursors for carbon–carbon bond formation reactions through Heck,⁷ Stille,⁸ and Suzuki⁹ transmetallation processes. Furthermore, bromoaromatics serve as potent antibacterial, antifungal, and antiviral agents, as well as industrial intermediates in the production of pharmaceuticals, agrochemicals, and other specialty products.^{10–20} Traditionally, bromination reactions are carried out using hazardous, toxic, and corrosive molecular bromine, often in combination with chlorinated solvents.^{21,22} This approach poses significant environmental and health risks due to mole-

cular bromine's toxicity and corrosive nature. Alternative methods involving electrophilic bromination using *N*-bromosuccinimide,^{23,24} alkyl bromide/sodium hydride/DMSO combinations,²⁵ bromodimethylsulfonium bromide²⁶ and a hexamethylenetetramine bromine complex²⁷ have been explored.

Oxidative bromination has emerged as an attractive and environmentally benign alternative, as it generates electrophilic bromine using various oxidants.^{28–34} This method offers a more sustainable and economically viable pathway to synthesize bromoaromatics compared to classical electrophilic substitutions. In particular, hydrogen peroxide is considered a promising oxidant for oxidative bromination, as the byproduct is only water. Most catalytic systems for oxidative bromination of arenes reported to date require acids,^{35–39} which, while inexpensive and readily available, pose challenges related to product separation and hazardous waste generation.^{40,41} Although oxidative bromination of arenes using bromide salts as halogen sources and oxidants has been explored,^{34,42–45} there remains a pressing need for low-cost, Earth-abundant, non-toxic catalysts that enable oxidative bromination with high yields and excellent regioselectivity under mild conditions.

Metal–organic frameworks (MOFs) have attracted considerable interest for developing robust single-site heterogeneous Earth-abundant catalysts for various applications owing to

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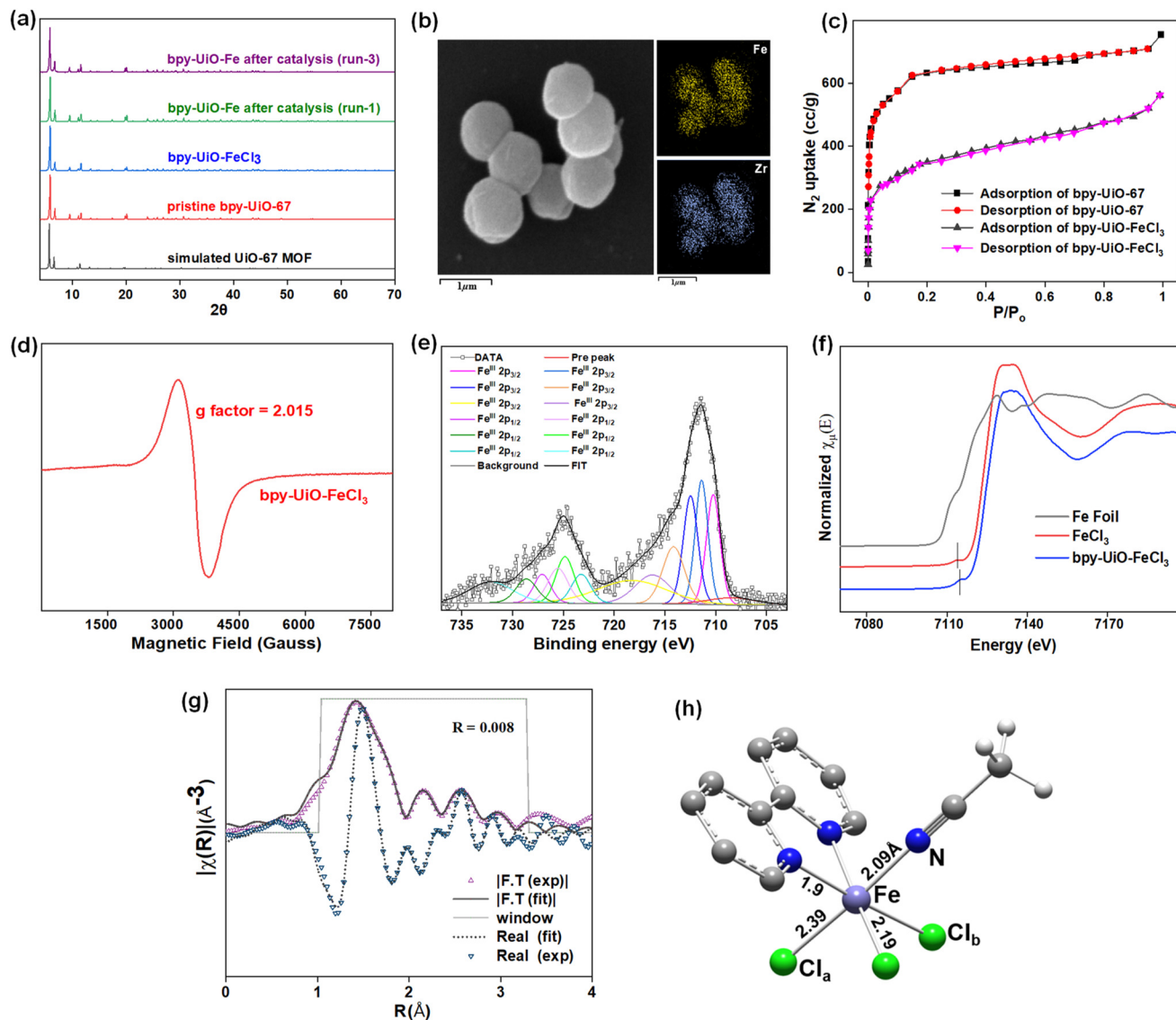


Fig. 2 (a) PXRD patterns of the simulated UiO-67 MOF (black), pristine bpy-UiO-67 (red), bpy-UiO-FeCl₃ (blue), bpy-UiO-Fe recovered after run-1 of oxidative bromination of aniline (green) and bpy-UiO-Fe recovered after run-3 of catalysis (purple). (b) SEM image of bpy-UiO-FeCl₃ particles along with elemental mapping of Fe and Zr. (c) N₂ sorption isotherms of bpy-UiO-67 (black/red)⁸³ and bpy-UiO-FeCl₃ (gray/magenta) measured at 77 K. (d) EPR spectrum of solid bpy-UiO-FeCl₃. (e) Fe 2p XPS spectrum of bpy-UiO-FeCl₃. (f) XANES spectra of metallic Fe(0) foil (gray), FeCl₃ (red) and bpy-UiO-FeCl₃ (blue). (g) EXAFS spectra and fits of bpy-UiO-FeCl₃ in the *R* space from 1.0 to 3.3 Å. (h) DFT-optimized structure of the bpy-UiO-FeCl₃(NCCH₃) moiety within bpy-UiO-FeCl₃ MOFs. The bond distances are given in Å.

Structure (XANES) analysis, the pre-edge energy of Fe in bpy-UiO-FeCl₃ closely matched that of FeCl₃ at 7114 eV, further confirming the presence of Fe³⁺ species (Fig. 2f). The X-band electron paramagnetic resonance (EPR) spectrum reveals a broad signal centered at *g* = 2.015, indicating the presence of a high-spin Fe³⁺ species with low magnetic anisotropy (Fig. 2d).^{84,85} Analysis of the Fe K-edge Extended X-ray Absorption Fine Structure (EXAFS) of bpy-UiO-FeCl₃ revealed that the Fe ion is octahedrally coordinated with two nitrogen atoms of bipyridine, three chloride ions, and one CH₃CN molecule (Fig. 2g). The Fe–N_{bipyridine} distance is 1.9 Å, while the Fe–Cl_a distance is 2.39 Å, the Fe–Cl_b distance is 2.19 Å and

the Fe–N_{CH₃CN} distance is 2.09 Å (Fig. 2h). The combined EXAFS and EPR data suggest the existence of a high-spin octahedral (bpy)Fe^{III}(Cl)₃(NCCH₃) species within bpy-UiO-FeCl₃.

Catalytic oxidative bromination of aniline

Bpy-UiO-FeCl₃ is an active heterogeneous catalyst for the oxidative bromination of aniline, utilizing H₂O₂ as the oxidant and KBr as the brominating agent. To optimize the reaction conditions for maximum conversion and yield, we thoroughly investigated the impact of various reaction parameters, including the reaction temperature, reaction time, solvents, substrate-to-oxidant ratio, catalyst concentration, and nature and

concentration of the brominating agent. The effect of temperature on the oxidative bromination of aniline was studied over a range of 30–60 °C using 1 mmol of aniline, 4 mg of the catalyst bpy-UiO-FeCl₃ (0.4 mol% of Fe), 2 mmol of H₂O₂, 1.1 mmol of KBr, and 5 mL of CH₃CN for a duration of 2 h (Fig. 3a). The results showed that temperature variation had only a minimal effect on the conversion of aniline; however, regioselectivity decreased at higher temperatures (entries 1–3, Table S2, ESI†). The reaction time plays a critical role in evaluating the catalytic performance of the catalyst. To investigate this, the effect of reaction time on the oxidative bromination of aniline with H₂O₂ was examined over a range of 30–180 min (Fig. 3b). The results showed a direct correlation between the reaction time and the yield of the 4-bromoaniline product. The highest yield of 95% was achieved after 2 h, indicating that longer reaction times enhance substrate interaction and conversion, enabling the catalyst to effectively promote the desired reaction. The study revealed that CH₃CN was the most efficient solvent for

the bpy-UiO-FeCl₃-catalyzed oxidative bromination of aniline using H₂O₂, achieving a conversion rate of 98% and a selectivity of 97% for the target product (2a) within 2 h (Fig. 3c). This enhanced performance is due to acetonitrile's beneficial solvation properties, which improve the stabilization of reaction intermediates and aid in the transfer of reactants at the catalyst's active sites.

In comparison, other solvents such as CH₃OH, DME and DCM resulted in lower yields of 2a. A control experiment confirmed the necessity of H₂O₂, as no bromo product was produced in its absence (entry 8, Table S2, ESI†). An investigation of different H₂O₂ concentrations, while keeping other parameters constant, revealed that maximum bromination was achieved at a 1:2 molar ratio (Fig. 3d). In contrast, a 1:3 molar ratio resulted in a decreased yield (81%) and reduced *para*-selectivity (82%). The effect of different brominating agents on the oxidative bromination of aniline using H₂O₂ as the oxidant was also investigated (Fig. 3e). Among the

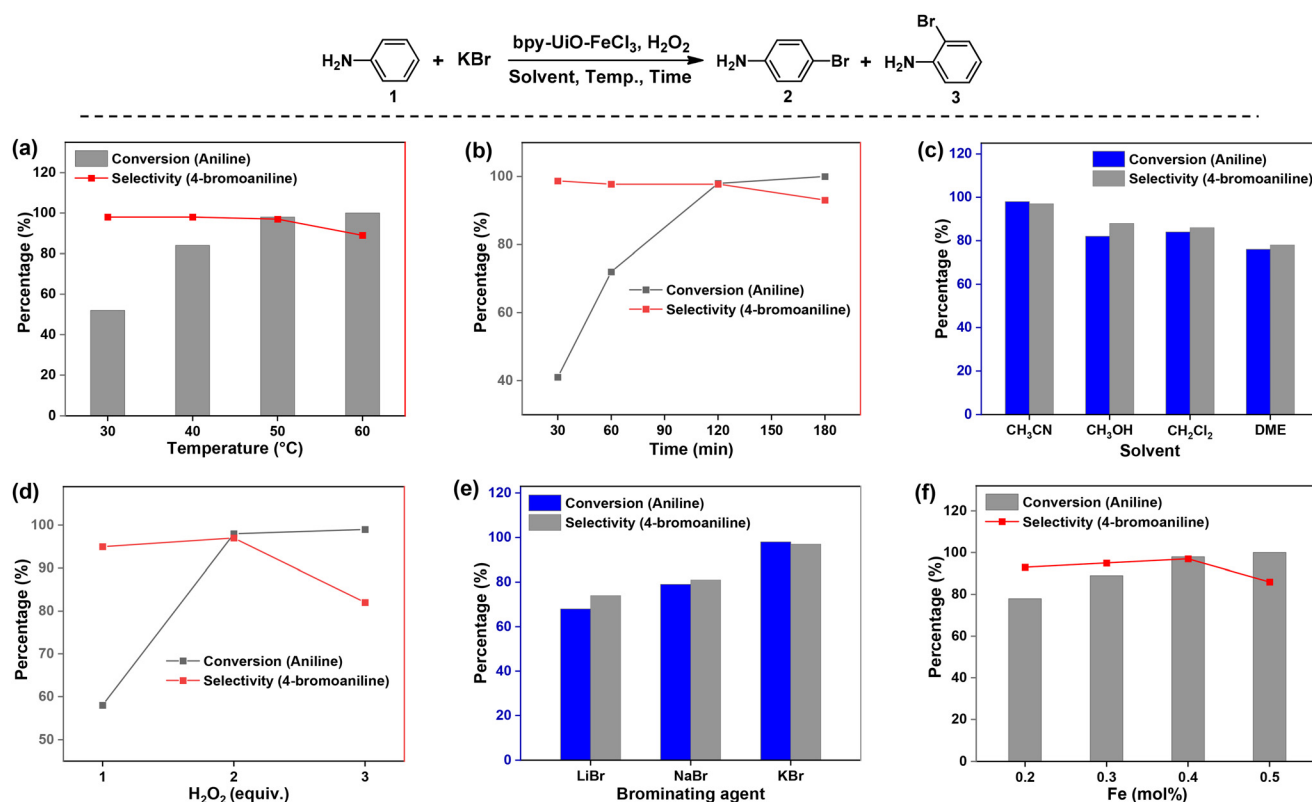


Fig. 3 (a) Effect of temperature on %conversion and %selectivity of 4-bromoaniline for bpy-UiO-FeCl₃-catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), CH₃CN (5 mL), 2 h. (b) Effect of time on %conversion and %selectivity of 4-bromoaniline for bpy-UiO-FeCl₃-catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), CH₃CN (5 mL), 50 °C. (c) Effect of different solvents on %conversion and %selectivity of 4-bromoaniline for bpy-UiO-FeCl₃-catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), solvent (5 mL), 50 °C, 2 h. (d) Effect of H₂O₂ amounts on %conversion and %selectivity of 4-bromoaniline for bpy-UiO-FeCl₃-catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), CH₃CN (5 mL), 50 °C, 2 h. (e) Effect of brominating agents on %conversion and %selectivity of 4-bromoaniline for bpy-UiO-FeCl₃-catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), H₂O₂ (2 mmol), brominating agent (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), CH₃CN (5 mL), 50 °C, 2 h. (f) Effect of different Fe loadings on %conversion and %selectivity of 4-bromoaniline for bpy-UiO-FeCl₃-catalysed oxidative bromination of aniline. Reaction conditions: aniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), CH₃CN (5 mL), 50 °C, 2 h.

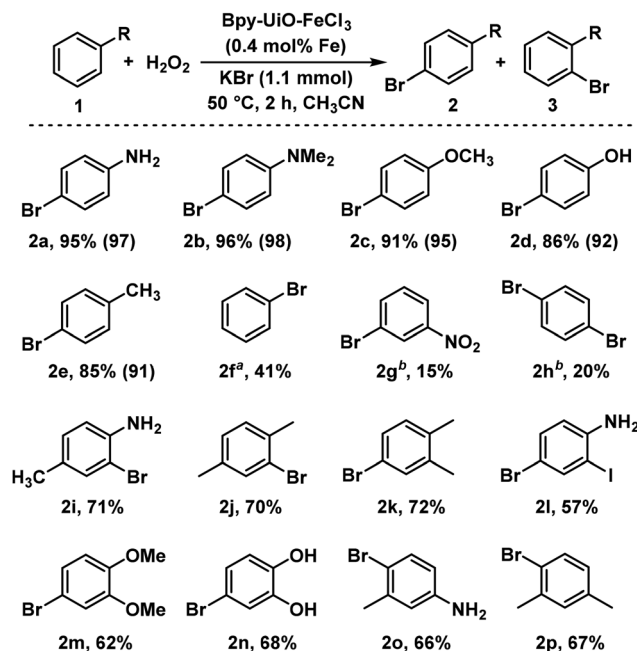
brominating agents tested (LiBr, NaBr, and KBr), KBr demonstrated the highest efficiency, achieving 98% conversion with excellent regioselectivity for the *para*-product (97%). In comparison, NaBr and LiBr showed lower activities (entries 11 and 12, Table S2, ESI†). A KBr concentration of 1.1 mmol yielded the optimal results. The catalyst loading was systematically optimized to achieve maximum efficiency. It was observed that 0.4 mol% of Fe loading in bpy-UiO-FeCl₃ provided the highest conversion rate of 98%. Reducing the Fe loading in the bpy-UiO-FeCl₃ catalyst from 0.4 mol% to 0.2 mol% resulted in a decline in bromoaniline yield from 95% to 73%, attributed to a reduced availability of active sites. Under the optimized conditions, the reaction achieved the highest yield of 4-bromoaniline (**2a**) at 95%. This was accomplished using a catalyst loading of 0.4 mol% Fe, 1 mmol of aniline, 1.1 mmol of KBr, and 2 mmol of 30% aqueous H₂O₂ in 5 mL of CH₃CN at 50 °C for 2 hours, resulting in a turn-over number (TON) of 238 (entry 2, Table S2, ESI†).

Substrate scopes for oxidative bromination of arenes

Under the optimized conditions, the oxidative bromination of aromatic substrates, including *N,N*-dimethylaniline (**1b**), anisole (**1c**), phenol (**1d**), and toluene (**1e**), afforded the corresponding *para*-bromo products (**2b–2e**) with isolated yields ranging from 85% to 96% and excellent selectivity (91–98%). Benzene (**1f**), due to its lack of activating groups, exhibited significantly lower conversion rates and required extended reaction times to achieve measurable bromination under the same conditions. In contrast, deactivated aromatic rings such as nitrobenzene (**1g**) and bromobenzene (**1h**) produced the corresponding bromo products with yields of 15–20% after 24 h at 80 °C. 4-Substituted aromatics, such as 4-methylaniline (**1i**) and *p*-xylene (**1j**), were selectively converted to 2-bromo-4-methylaniline (**2i**) and 2-bromo-*p*-xylene (**2j**) with isolated yields of 70–71%. In contrast, 2-substituted aromatics such as *o*-xylene (**1k**), 2-iodoaniline (**1l**), 1,2-dimethoxybenzene (**1m**) and catechol (**1n**) were also selectively converted to the corresponding bromo products (**2k–n**) with isolated yields of 57–72%. Similarly, 3-substituted aromatics such as 3-methylaniline (**1o**) and *m*-xylene (**1p**) were selectively converted to 4-bromo-3-methylaniline (**2o**) and 4-bromo-*m*-xylene (**2p**), respectively, achieving yields of 66–67% under the same conditions (Scheme 1).

Control experiments

Bpy-UiO-FeCl₃ acts as a heterogeneous catalyst and can be recycled at least three times while maintaining consistent activity (Fig. 4a). The PXRD pattern of the recovered MOF material after catalysis revealed no apparent change in crystallinity and structure of the MOFs (Fig. 2a). The percentage of leached Fe and Zr into the supernatant after the first run was 0.02% and 0.6%, respectively, while after the third run, it was 0.08% and 1.5%, as analyzed by ICP-OES (Table S5, ESI†). The catalytic activity of bpy-UiO-FeCl₃ is over four times greater than that of the homogeneous control, bipyridine-FeCl₃. The latter was synthesized by reacting 5,5'-dimethyl-2,2'-bipyridine



Scheme 1 Substrate scope of oxidative bromination of arenes with bpy-UiO-FeCl₃. Conditions: **1** (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), bpy-UiO-FeCl₃ (4 mg, 0.4 mol% of Fe), CH₃CN (5 mL), 50 °C, 2 h. Yields refer to the isolated products. Selectivity of *para*-bromo products is given in parentheses. ^aThe reaction was performed for 10 h. ^bThe reaction was performed for 24 h at 80 °C.

with FeCl₃·6H₂O in a 1 : 1 molar ratio in THF. The time evolution plot for bpy-UiO-FeCl₃ (0.4 mol% of Fe) catalyzed oxidative bromination of aniline demonstrates a linear increase in the synthesis of 4-bromoaniline, achieving 97% selectivity until 98% conversion of aniline in 2 h (Fig. 4b). In contrast, under the same reaction conditions and with equivalent Fe loading, bipyridine-FeCl₃ produced only 26% yield of 4-bromoaniline in 2 hours, with a selectivity of 68% (Fig. 4b). This enhanced activity of the bpy-UiO-FeCl₃ MOF is attributed to the stability of bpy-FeCl₃ species, which are isolated at the linkers, preventing decomposition.

In addition, the bpy-UiO-FeCl₃ framework features uniform and rigid pores with a size of 0.68 nm, which allow the diffusion of aniline (0.83 × 0.67 nm) and *p*-bromoaniline (0.97 × 0.67 nm); however, they restrict the formation of the larger product, *o*-bromoaniline (0.88 × 0.79 nm), resulting in the formation of *p*-bromoaniline with 97% selectivity through shape-selective catalysis. While the MOF pores (0.68 nm) are indeed identical to or smaller than the reported molecular widths of aniline (0.83 × 0.67 nm) and *para*-bromoaniline products (0.97 × 0.67 nm), molecules are not rigid and can reorient or deform during diffusion and enter the pore by aligning its narrower axis (0.67 nm) with the pore window.⁷⁶ In contrast, the homogeneous bipyridine-FeCl₃ catalyst lacks this structural confinement, leading to only 68% selectivity of *p*-bromoaniline. To confirm that the oxidative bromination reaction occurs predominantly within the pores of the bpy-UiO-FeCl₃ MOF, rather

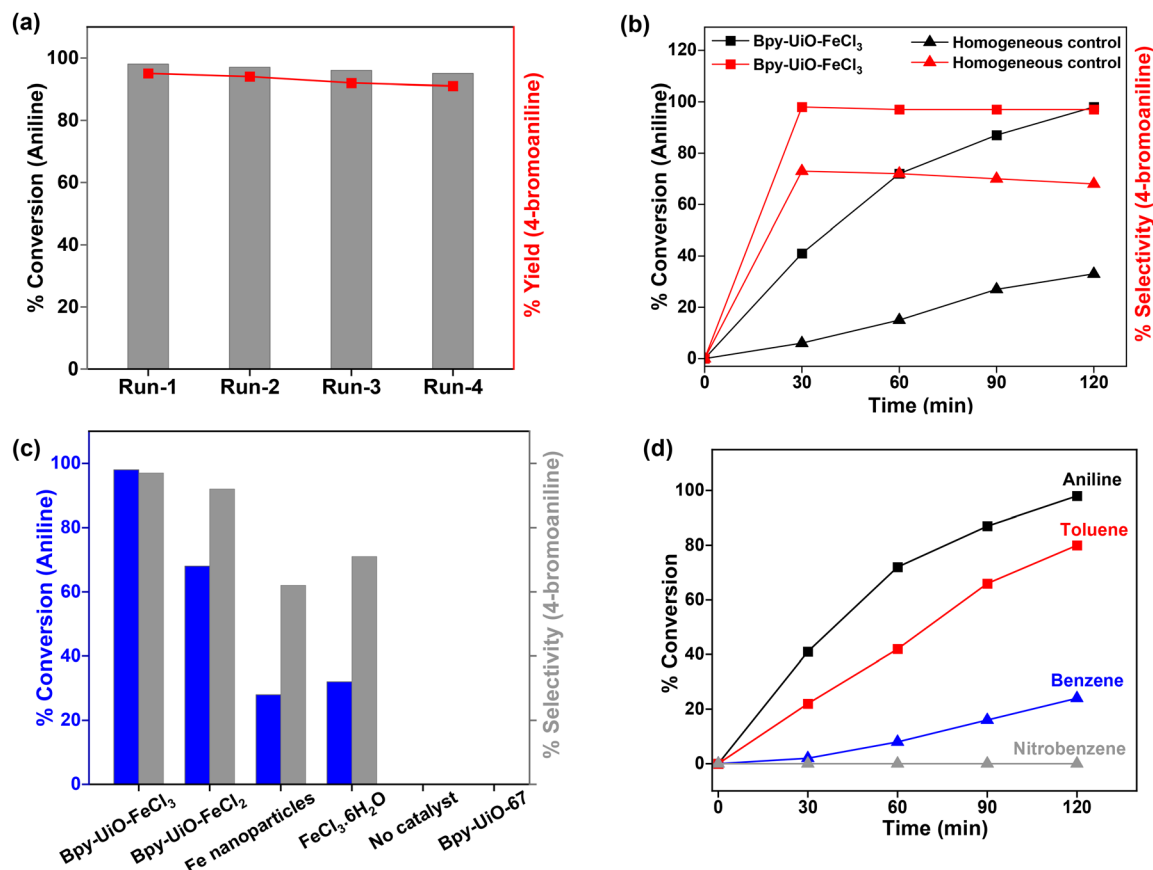


Fig. 4 (a) Plot for the %conversion of aniline and the %yield of 4-bromoaniline at various runs in the recycling of bpy-UiO-FeCl₃-catalyzed oxidative bromination of aniline. (b) Time evaluation studies of oxidative bromination of aniline using bpy-UiO-FeCl₃ and its homogeneous control [(bpy) FeCl₃] under identical conditions. Conditions: aniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), catalyst (0.4 mol% of Fe), CH₃CN (5 mL), 50 °C. (c) Comparison of the catalytic activity of bpy-UiO-FeCl₃ with other iron catalysts under identical reaction conditions. Conditions: aniline (1 mmol), H₂O₂ (2 mmol), KBr (1.1 mmol), catalyst (0.4 mol% of Fe), CH₃CN (5 mL), 50 °C, 2 h. (d) Time evaluation studies of oxidative bromination of aniline, toluene, benzene and nitrobenzene under the optimized reaction conditions.

than on the external surface of the MOF, an experiment was conducted using a bulky phosphine, tricyclohexylphosphine, to block the surface iron active sites.^{74,76} The addition of 1.2 equivalents of tricyclohexylphosphine per iron ion in the bpy-UiO-FeCl₃-catalyzed oxidative bromination of aniline resulted in a slight decrease in conversion to ~88%. However, the regioselectivity for the *para*-bromoaniline product remained unchanged (97%). This observation suggests that the iron active sites are mostly embedded within the MOF pores, which catalyze the oxidative bromination of arenes within the pores (entry 8, Table S3, ESI†). Several controlled experiments were conducted to identify the actual catalytic species involved in the bpy-UiO-FeCl₃-catalyzed oxidative bromination of aniline to produce 4-bromoaniline. The results showed that reactions (a) without the bpy-UiO-FeCl₃ catalyst (entry 3, Table S3†) and (b) with the pristine bpy-UiO-67 MOF (entry 2, Table S3†) all yielded negligible amounts of 4-bromoaniline. The results also showed that reactions (a) with bpy-UiO-FeCl₂ (entry 4, Table S2†), (d) with FeCl₃·6H₂O (entry 5, Table S2†) and (e) with Fe nanoparticles (entry 6, Table S2†) all yielded lower amounts of 4-bromoaniline with less selectivity (Fig. 4c). This

confirms that bpy-UiO-FeCl₃ is the active catalyst for the oxidative bromination of aniline. The oxidative bromination of aniline ceased upon the removal of the solid MOF catalyst, indicating that the active species is embedded in the MOF solid (section 3.4, ESI†).

Mechanism exploration of bpy-UiO-FeCl₃-catalyzed oxidative bromination of aniline

The mechanism of bpy-UiO-FeCl₃-catalyzed oxidative bromination of aniline was investigated by characterizing the catalyst after catalysis and computational studies. The PXRD pattern of the recovered bpy-UiO-Fe MOF after catalysis indicates that both the structure and crystallinity of the MOF remained intact during the reaction (Fig. 2a). Additionally, the absence of any characteristic peak for metallic iron at higher 2θ angles in the same PXRD pattern suggests that Fe(0) nanoparticles or metallic Fe particulates did not form during the bromination reaction. The XPS analysis of bpy-UiO-FeCl₃ after oxidative bromination of aniline identified Fe 2p_{3/2} and 2p_{1/2} binding energy peaks at 711.8 eV and 724.6 eV, respectively, confirming the +3 oxidation state of the iron ion (Fig. S12, ESI†). Again,

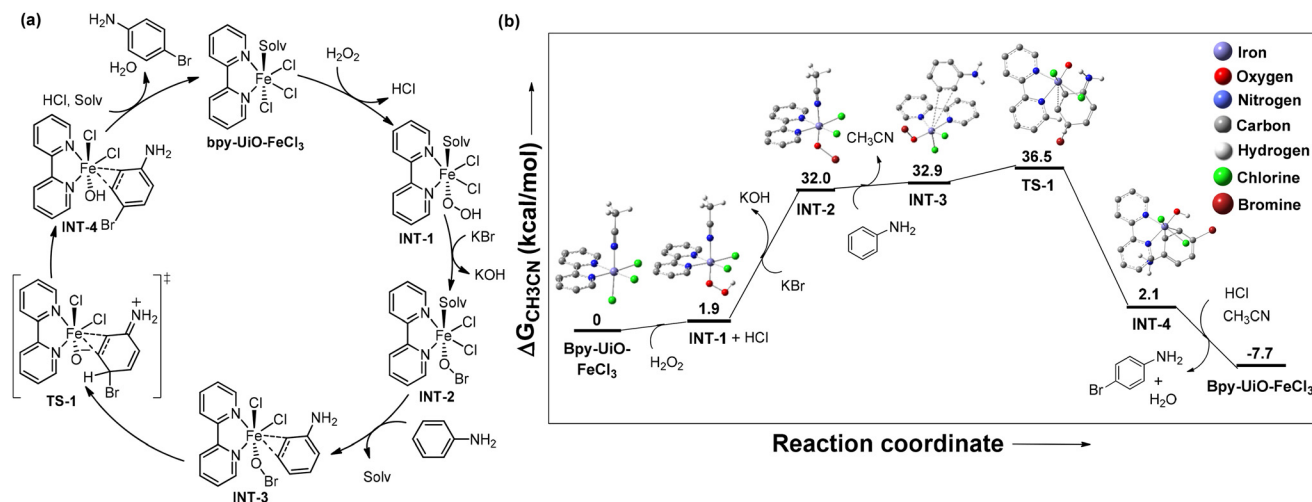


Fig. 5 (a) Proposed catalytic cycle of bpy-UiO-FeCl_3 -catalyzed oxidative bromination of arenes. (b) DFT-calculated free energy profile diagram of bpy-UiO-FeCl_3 -catalyzed oxidative bromination of aniline at 323.15 K.

radical pathway tests utilizing Na_2SO_3 and *tert*-butanol (TBA) as scavengers demonstrated no impact on the reaction rate, effectively ruling out the possibility of a radical mechanism (Fig. S6, ESI†).

Based on spectroscopic data and control experiments, we propose that the reaction of H_2O_2 with bpy-UiO-FeCl_3 initially forms an Fe(III)-hydroperoxy intermediate, $[\text{Fe}^{\text{III}}(\text{OOH})]$ (INT-1). Subsequently, the Br^- ion from KBr attacks the oxygen atom coordinated to iron in INT-1, forming the $[\text{Fe}^{\text{III}}(\text{OBr})]$ intermediate (INT-2) and releasing KOH . INT-2 interacts with the aniline substrate to form INT-3, where electrophilic aromatic substitution takes place. The reactive Br^+ then undergoes an electrophilic attack on the aniline substrate, resulting in the formation of the bromoaniline-bound Fe(III) intermediate (INT-4) via transition state 1 (TS-1). Finally, the desired p -bromoaniline product is released from INT-4, regenerating the initial Fe(III) catalyst, bpy-UiO-Fe , and completing the catalytic cycle (Fig. 5a).

Evidence for the electrophilic aromatic substitution mechanism was gathered through a time-evolution study of reactions involving arenes such as aniline, toluene, benzene, and nitrobenzene under identical conditions (Fig. 4d). The reaction rates followed the trend aniline > toluene > benzene, consistent with the activating effects of electron-donating groups. In contrast, nitrobenzene did not undergo the reaction due to the deactivating influence of its electron-withdrawing nitro group, rendering the aromatic system unreactive under these conditions.

To gain a deeper understanding of the reaction pathway, we computed the entire catalytic cycle using Density Functional Theory (DFT) at the B3LYP/def2-SVP/SMD (solvent = acetonitrile) level of theory in Gaussian 09 software (Fig. 5b). The DFT-calculated free energy diagram at 323.15 K for the bpy-UiO-FeCl_3 -catalyzed oxidative bromination of aniline indicates that the coordination of H_2O_2 with the bpy-UiO-FeCl_3 MOF is

endergonic by $1.9 \text{ kcal mol}^{-1}$. Furthermore, nucleophilic substitution of Br^- on $[\text{Fe}^{\text{III}}(\text{OOH})]$ leading to the formation of $[\text{Fe}^{\text{III}}(\text{OBr})]$ species (INT-2) is endergonic by $30.1 \text{ kcal mol}^{-1}$. In the next step, the conversion of INT-2 to INT-3 is endergonic by $0.9 \text{ kcal mol}^{-1}$. The subsequent transformation of INT-3 to INT-4 via TS-1 is exergonic by $34.4 \text{ kcal mol}^{-1}$, overcoming a barrier of $3.6 \text{ kcal mol}^{-1}$. Finally, the release of p -bromoaniline from INT-4 regenerates the bpy-UiO-Fe MOF, which is exergonic by $9.8 \text{ kcal mol}^{-1}$. DFT calculations suggest that the nucleophilic substitution of Br^- on INT-1 leading to the formation of INT-2 is the turnover limiting step requiring a free activation energy of $30.1 \text{ kcal mol}^{-1}$ (Fig. 5b).

Conclusions

In summary, we have successfully synthesized a porous and highly robust zirconium-based metal-organic framework (MOF)-supported mono-bipyridyl-iron(III) chloride catalyst through active-site isolation. Bpy-UiO-FeCl_3 demonstrates high selectivity and recyclability for the oxidative bromination of various substituted arenes using hydrogen peroxide (H_2O_2) as the oxidant and potassium bromide (KBr) as the bromine source. Mono-substituted arenes were converted to *para*-bromoarenes with excellent selectivities ranging from 90% to 98%. The uniform and regular porous structure of the MOF facilitates shape-selective catalysis, preventing the formation of larger *ortho*-bromoarene products, ensuring the exclusive formation of *para*-bromoarenes, unlike homogeneous catalysts that typically exhibit lower selectivity. Bpy-UiO-FeCl_3 is also effective for a wide range of 1,2-, 1,3-, and 1,4-substituted arenes, converting them into the desired bromo products with moderate to good yields under mild reaction conditions. Through spectroscopic and computational studies, we investigated the mechanism and identified the turnover-limiting step

in the catalytic cycle. Our findings highlight the importance of MOFs in creating sustainable, Earth-abundant metal catalysts for the direct oxidative bromination of arenes, enabling the eco-friendly synthesis of haloarenes.

Author contributions

R. K. and A. K. synthesized the MOF catalyst and performed catalytic reactions. P. G. performed the DFT calculations. R. K., B. R., B. S. and M. C. characterized the MOF materials and analyzed the data. K. M. designed and supervised the entire project. K. M. and R. K. wrote the manuscript. All the authors approved the final version of the manuscript.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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