

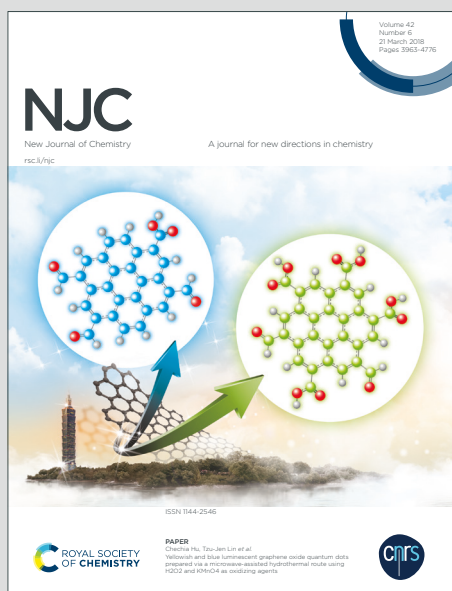
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## ARTICLE

## Polyamine Dendritic Polymer–Copper Complex: A Reusable Catalyst for Additive-Free Amination of Aryl Bromides, and Iodides

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A porphyrin initiated amine-functionalized polyepichlorohydrin dendritic polymer (PPECH-Amine) was effectively synthesized and its water-soluble copper complex (PPECH-Amine-Cu) was developed by treating with copper acetate. The PPECH-Amine and PPECH-Amine-Cu were characterised by different spectroscopic and microscopic techniques. The PPECH-Amine-Cu was identified as a reusable catalyst for the amination of bromo and iodo benzene derivatives in aqueous media. Due to the presence of residual amino groups in PPECH-Amine-Cu catalyst, the protocol does not need any additional base additive as ammonia itself acts as base and coupling partner. Due to the good water-soluble nature of this catalyst, it can be easily separated and reused up to six reaction cycles without any loss of its activity.

### Introduction

The nature of ligand is an indispensable feature of stabilizing active metals in organometallic, homogeneous catalysis.<sup>1–4</sup> The ligand regulates the coordination position of the metal capable of attaching and detaching the reactant and product, respectively.<sup>5,6</sup> Furthermore, examples are known in which ligands enhance reaction rates by changing and partaking within the catalytic cycle.<sup>7,8</sup> The highly stable complex of the ligand with the metal will diminish its catalytic activity.<sup>9</sup> Hence, a mild and stable ligating agent for the organometallic catalyst is yet in demand. By the deep literary critique, it came to perceive that dendritic polymers were very good ligating agents and form metal complexes effectively.<sup>10–14</sup> There are many examples which had unveiled the catalytic activity of dendritic polymers.<sup>15–19</sup>

The last decade had witnessed an upsurge in palladium-catalyzed C-C, C-N and C-O bond-forming cross-coupling reactions of aryl halides as remarkably effectual synthetic tools,<sup>20–23</sup> in which C-N bond formation was an important step for the synthesis of aromatic amines from the corresponding bromo/iodobenzene. Aromatic amines are essential starting materials for the production of

agrochemicals, pharmaceuticals, dyes, pigments, and rubber.<sup>24–28</sup> The traditional palladium catalyzed direct amination of alkyl halides have high cost and toxicity obstacles, which limit their massive applications of industrial scales.<sup>29–32</sup> The cost problems can be solved by copper-catalyzed direct amination, but it needs high temperature,<sup>33,34</sup> and a stoichiometric amount of copper which cause environmental issues.<sup>35,36</sup> So the development of reusable copper catalyst is of significance. In 2003 Batey and Quach demonstrated a ligand and base-free copper(II)-catalyzed C-N bond formation of organoboron compounds with aliphatic amines and anilines.<sup>37</sup> In 2008 Chang et al. first reported a copper based catalytic system for the amination of aryl halides using aqueous ammonia solution.<sup>38</sup> Dawei Ma et al. explored the extremely effective oxalic diamide ligands with CuI in the amination of less reactive (hetero)aryl chlorides under mild conditions. The same group had extended their work with the development of Cu<sub>2</sub>O/MNBO-catalyst system with less catalyst loading (only 0.1–0.5 mol %) and high turnover value (over 10000).<sup>39–41</sup> Recently, Takagi et al reported a simple protocol for copper-catalyzed arene amination using aqueous ammonia.<sup>42</sup> Most of the above mentioned catalyst systems needed a base additive like Cs<sub>2</sub>CO<sub>3</sub>, K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> etc.<sup>43–45</sup>

Here, the synthesis and evaluation of the catalytic efficiency of amine functionalised Polyepichlorohydrin-copper complex (PPECH-Amine-Cu) was demonstrated for the additive-free synthesis of primary aromatic amines by the cross-coupling reaction of aryl bromides, and iodides with ammonia in aqueous medium. The PPECH-Amine-Cu acted

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twofold; as a copper source and as a base for reductive elimination.

## Experimental

### Synthesis of porphyrin cored polyepichlorohydrin (POR-PECH)

In a 250 mL three necked flask equipped with a mechanical stirrer and a nitrogen inlet, 5, 10, 15, 20-tetrakis (3,4-dihydroxyphenyl)porphyrin (3.71 g, 5 mmol) was dissolved in 20 ml of THF. Boron trifluoride etherate (6.48 mL, 40 mmol) was added and the mixture was stirred for 30 min. To this solution, epichlorohydrin (27.8 mL, 300 mmol) was added using a dropping funnel along with vigorous stirring for 3h. The reaction was quenched by pouring 50 mL of water into the reaction flask. The resulting mixture was washed several times with dichloromethane and separated using a separating funnel. The dichloromethane layer along with the product was dried over magnesium sulphate. The solvent was removed using a rotary vacuum evaporator

### Conversion of porphyrin cored polyepichlorohydrin to polyazide

To the warm mixture of Sodium azide (1.52 g) and Lithium chloride in DMSO (5 mL), POR-PECH (3 g) was added with stirring at 110 °C. The mixture was stirred at the same temperature for three days. The crude mixture was extracted in chloroform and the excess reagent was washed with hot water. The organic layer was separated using a separating funnel. The solvent was removed under vacuum to obtain the polyazide.

### Conversion of polyazide to polyamine (PPECH-Amine)

In a 100 mL R. B. flask equipped with a mechanical stirrer, 3g polyazide dissolved in 10 mL of dry THF, was taken and the reaction mixture was cooled to 0 °C. To this solution, LiAlH<sub>4</sub> in THF was added with vigorous stirring using a dropping funnel. The mixture was vigorously stirred at 0 °C for 4 h, and the temperature was allowed to rise to room temperature. It was filtered using methanol and the excess solvent was evaporated under vacuum.

### Conversion of polyamine to polyamine copper complex (PPECH-Amine-Cu)

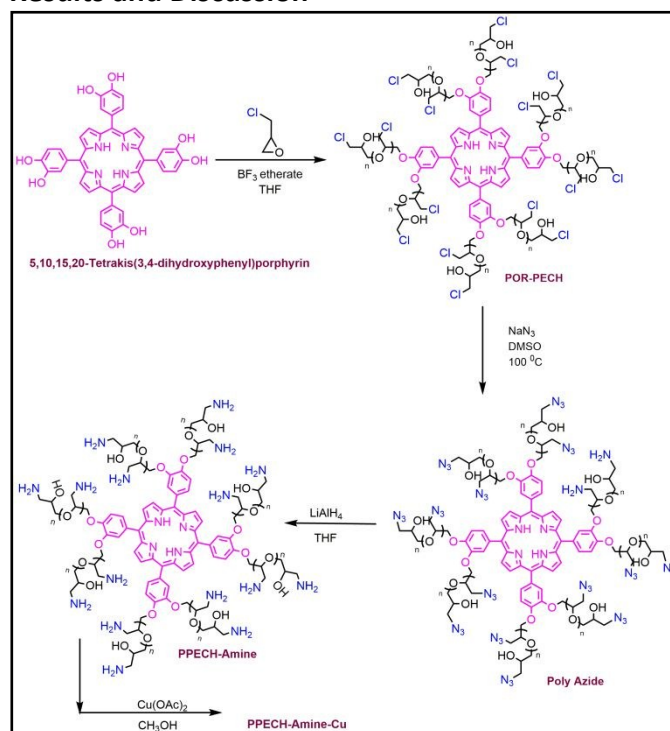
A 50 mL round bottom flask was loaded with 3 g of PPECH-Amine dendritic polymer. A standard aqueous solution of the copper acetate (30 mL, 0.03 M) was added to the flask. The reaction mixture was stirred at room temperature for 36 h. After completion of the reaction, the PPECH-Amine-Cu complex was subjected to centrifugation. Washing of the sedimented PPECH-Amine-Cu complex several times by deionised water yielded pure green coloured water-soluble gel-type PPECH-Amine-Cu complex.

### General procedure for the amination of aryl halides

PPECH-Amine-Cu catalyst (0.3 mol%), and 4-bromoanisole (3 mmol) were charged in a 10 mL R. B. flask, and 10 mL of 0.5

M ammonia solution and 5 mL of water were added. The reaction mixture was stirred at room temperature for 9 h. The completion of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with ethylacetate and washed three times with water (20 mL × 3). The combined organic layer was dried over sodium sulphate, and evaporated in rotary vacuum evaporator to get pure amine derivatives. The centrifugation of aqueous layer resulted in the separation of catalyst.

## Results and Discussion



Scheme 1. Synthesis of PPECH-Amine-Cu complex

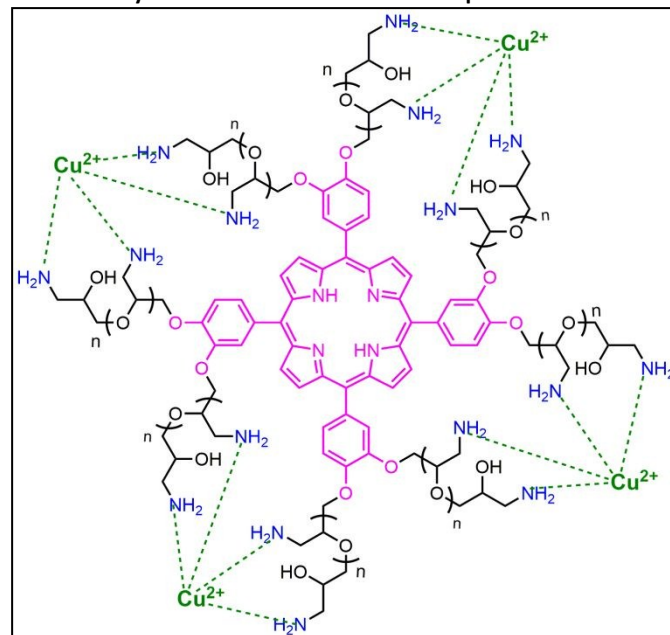


Fig.1: Structure of PPECH-Amine-Cu

PPECH-Amine (Fig.1.) was synthesized as per the procedure given in the scheme.1. The 5,10,15,20-tetrakis(3,4-dihydroxyphenyl)porphyrin initiated ring opening polymerisation (ROP) of epichlorohydrin resulted in the formation of porphyrin cored polyepichlorohydrin dendritic polymer (POR-PECH).<sup>46</sup> The free chlorine groups of the POR-PECH were converted to azide using sodium azide, subsequent reduction of azide groups led to the formation of PPECH-Amine. The amine capacity of POR-G0 was found to be 287.21 mmol/g by titration method. The structure and effective polymerisation of PPECH-Amine was confirmed by UV-Vis, FT-IR, NMR, FE-SEM, GPC, and TG techniques. The treatment of PPECH-Amine with copper acetate resulted in a green coloured water-soluble gel type polyamine dendritic polymer-copper complex (PPECH-Amine-Cu). The metal content and the oxidation states of copper in PPECH-Amine-Cu were analysed by ICP/OES, EDX, and XPS analysis.

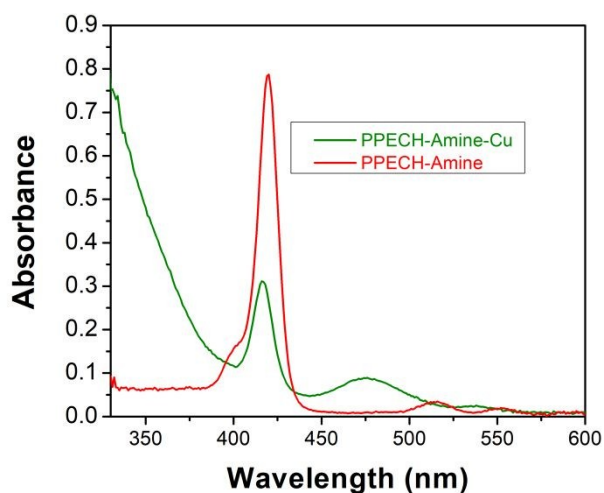


Fig. 2: UV-Vis spectrum of PPECH-Amine (Red) and PPECH-Amine-Cu complex (Green)

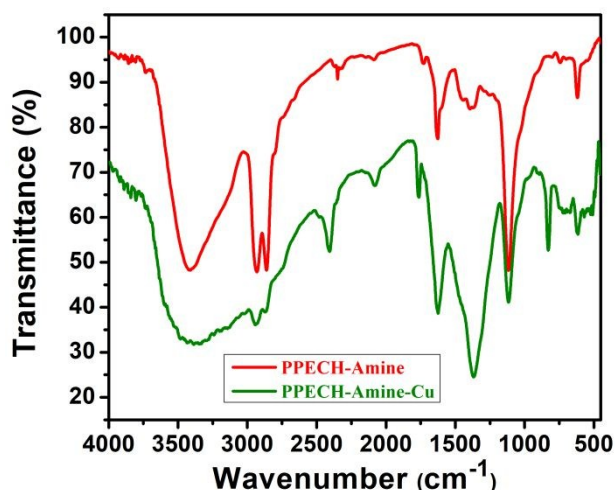


Fig. 3: FT-IR spectrum of PPECH-Amine (Red) and PPECH-Amine-Cu complex (Green)

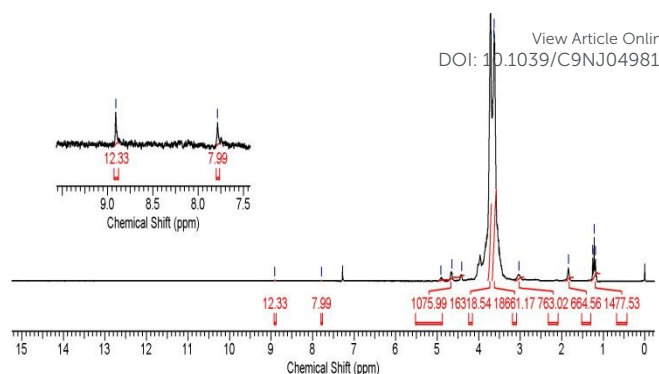


Fig. 4: <sup>1</sup>H NMR spectrum of PPECH-Amine-Cu complex

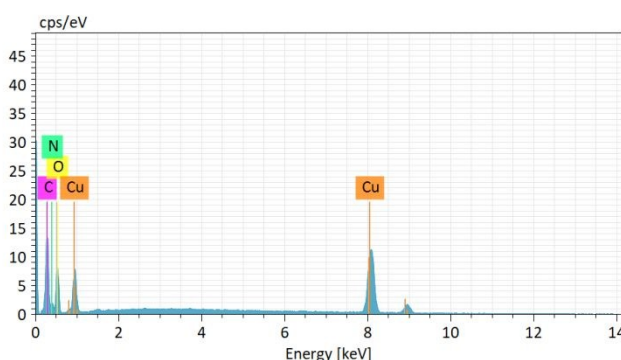


Fig. 5: EDX patterns of PPECH-Amine-Cu complex

The UV-Vis spectrum of PPECH-Amine-Cu (Fig.2) contained soret band near 418 nm and generation of new peak at 472 nm depicted the porphyrin moiety and the formation of copper complex. In the FT-IR spectrum (Fig.3) broadening of band near 3400  $\text{cm}^{-1}$  after addition of copper gave more insight to the formation of copper complex. The <sup>1</sup>H NMR spectrum of PPECH-Amine-Cu showed small peaks at 7.8 and 8.9 ppm which confirmed the porphyrin core. The multiplets around 3.2 - 4.1 confirmed the alkoxy dendritic chains (Fig.4). High loading of copper in the dendritic polymer was analysed by ICP/OES technique and found to be 19.39 %. The EDX spectrum established the presence of C, N, O and Cu in PPECH-Amine-Cu catalyst. From the ICP/OES and EDX analysis, the high loading of copper in PPECH-Amine-Cu was confirmed.

To understand the oxidation state of copper in PPECH-Amine-Cu catalyst, the XPS technique was adopted. In the XPS image (Fig. 6a and 6b) the peak at 961.4 eV corresponded to the  $2p_{1/2}$  ( $3d^9$ ) atmosphere, which confirmed the presence of  $\text{Cu}^{2+}$  in the dendritic polymer. The strong shake up satellite peaks at 940 and 942.6 eV were observed due to the presence of unpaired electron in open  $3d^9$  shell of  $\text{Cu}^{2+}$  which supported the paramagnetic chemical state of  $\text{Cu}^{2+}$  in PPECH-Amine-Cu catalyst.<sup>47,48</sup> Moreover, the binding energy difference between  $\text{Cu}2p_{3/2}$  and  $\text{Cu}2p_{1/2}$  peaks turned out to be 19.9 eV. In previous reported works,<sup>49-51</sup> the energy separation of  $\geq 19.8$  eV was observed in  $\text{Cu}^{2+}$ , whereas  $\leq 19.8$  eV was attributed to either pure metallic Cu or  $\text{Cu}^+$ .

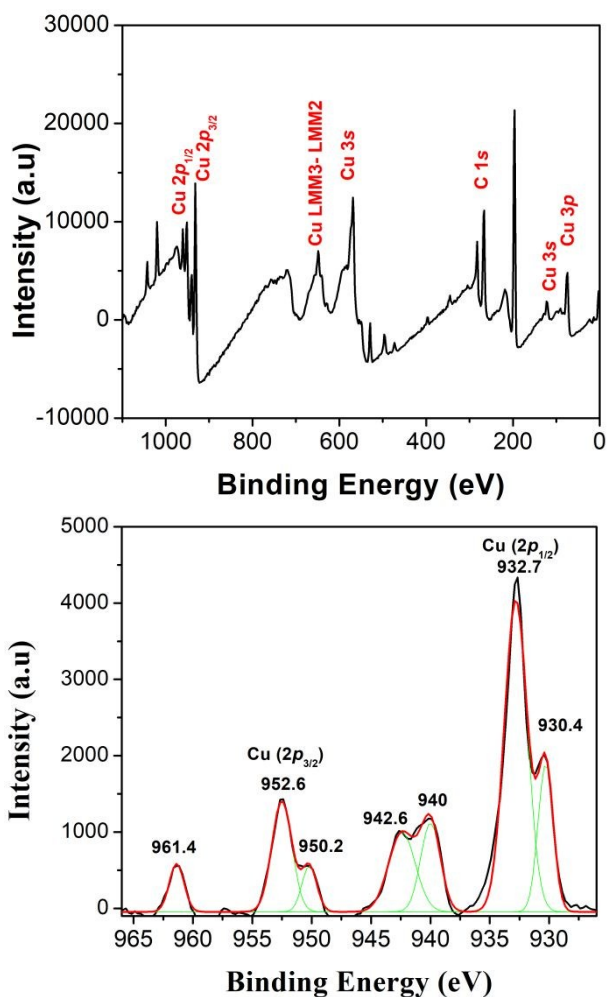


Fig. 6: XPS spectrum of PPECH-Amine-Cu complex

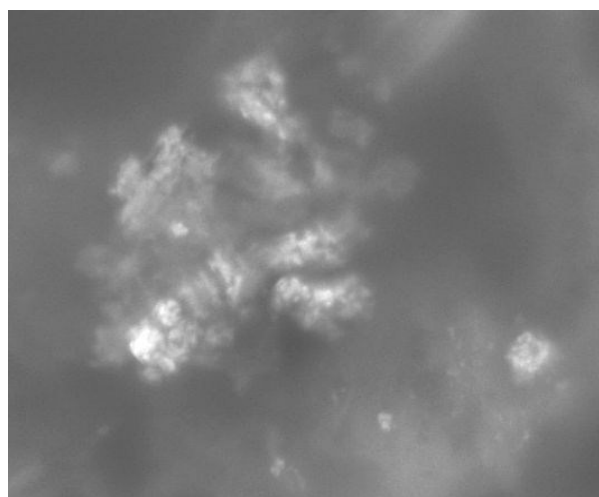


Fig. 7A: FE-SEM image of PPECH-Amine dendritic polymer

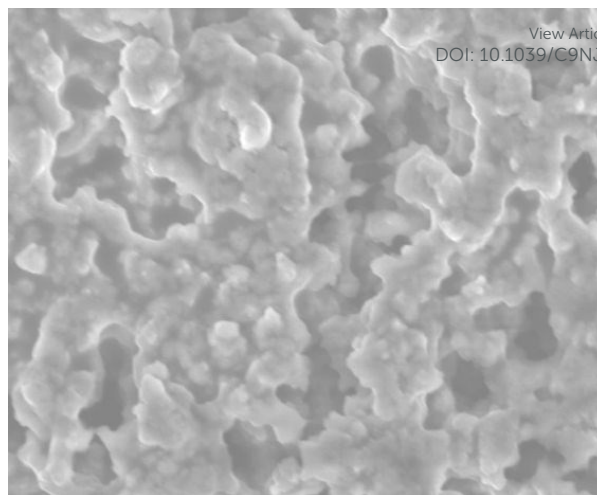


Fig. 7B: FE-SEM image of PPECH-Amine-Cu complex

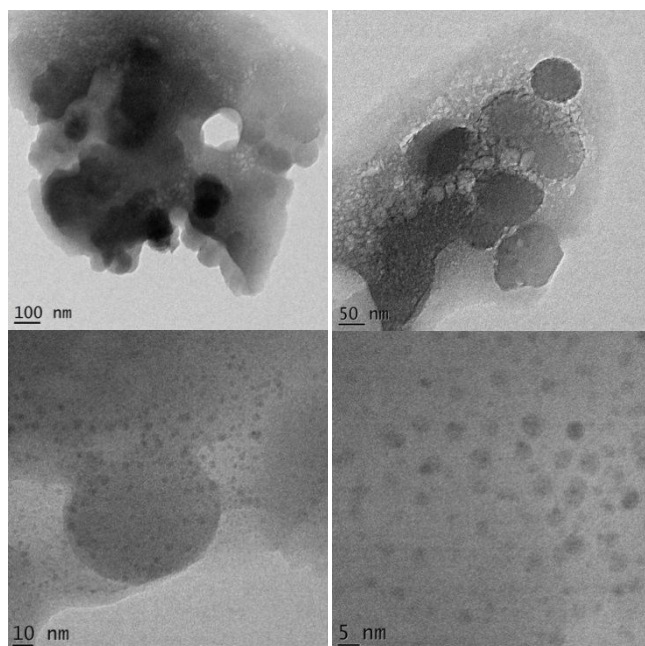


Fig. 8: FE-TEM image of PPECH-Amine-Cu complex

The field emission scanning electron microscopy (FE-SEM) image of PPECH-Amine dendritic polymer (Fig.7A) confirmed the spherical morphology. After complexation with copper, it underwent an aggregation which resulted in a gel type morphology (Fig.7B). In order to gain deeper insight into the spherical structure of the PPECH-Amine-Cu catalyst, it was analyzed using high resolution transmission electron microscopy (HR-TEM). It confirmed the packing of 3-5 nm sized copper aggregates inside and the periphery consisted of spherical-shaped dendritic polymer particles in 60–100 nm size range (Fig.8).

The thermal stability of the synthesised PPECH-Amine-Cu catalyst was analysed by TG-DTG analysis (Fig.9). The decomposition temperature of the catalyst was found to be 220 °C, which marked it as a potential catalyst for high temperature chemical reactions. The broad peaks in the PXRD image (Fig.10) revealed the semi crystalline nature of the PPECH-Amine-Cu.

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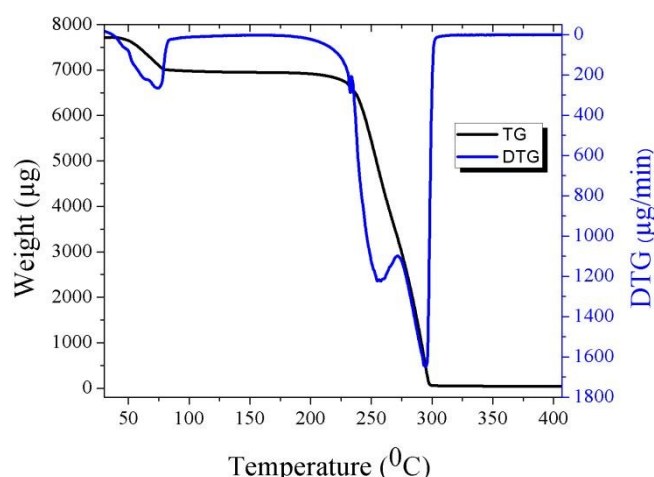


Fig. 9: TG-DTG Traces of PPECH-Amine-Cu complex

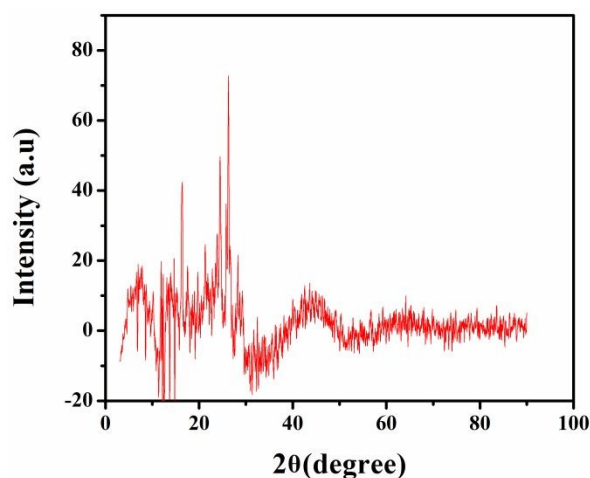
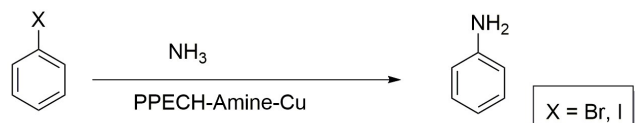


Fig. 10: PXRD Image of PPECH-Amine-Cu complex

### Evaluation of catalytic activity

The catalytic activity of synthesized PPECH-Amine-Cu complex was evaluated in direct amination of aryl halides, given in the scheme 2 using ammonia solution as the nitrogen source. Further studies revealed that 0.3 mol% PPECH-Amine-Cu catalyst was enough for the amination of 3 mmol of aryl halide.



Scheme 2: Synthesis of aryl amines from aryl halides

To optimize the reaction conditions for the direct amination process, 4-bromoanisole was selected as the model substrate. Several amine sources like  $\text{NH}_4\text{OAc}$ ,  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{NH}_3$  solutions were screened and the best activity was observed for ammonia solution. The reaction was conducted in different solvents and water was found to be the best one due to the high water soluble nature of both the catalyst and ammonia. The solvent optimisation results are tabulated in table 1.

Generally, the direct amination of aryl halides required a base additive. In order to analyse the effect of base in this reaction, different bases were attempted and the results are tabulated in table 2. From the table 2, it was inferred that the introduction of base did not alter the reaction yield. Even without the base additive, the protocol produced excellent yield. It may be due to the presence of free amino groups in PPECH-Amine-Cu catalyst,<sup>52,53</sup> which acted as a base for the direct amination process.

Table 1: Optimization of Solvent

Sl. No.	Solvent	Yield (%)
1	Toluene	45
2	$\text{CH}_3\text{CN}$	60
3	Chloroform	55
4	Dichloromethane	56
5	Methanol	90
6	Ethanol	91
7	Water	96

(Reactions conducted with 3 mmol 4-bromoanisole, 10 mL of 0.5 M ammonia solution, 3.5 mmol Sodium tert-butoxide, 0.3 mol % PPECH-Amine-Cu catalyst, room temperature, 12h.)

Table 2: Optimization of Base

Sl. No.	Base (3.5 mmol)	Yield (%)
1	Sodium tert-butoxide	96
2	$\text{Cs}_2\text{CO}_3$	80
3	$\text{NaOH}$	96
4	$\text{K}_2\text{CO}_3$	77
5	$\text{K}_3\text{PO}_4$	82
6	Without any Base	96

(Reactions conducted with 3 mmol 4-bromoanisole, 10 mL of 0.5 M ammonia solution, 0.3 mol % PPECH-Amine-Cu catalyst, room temperature, 12h, in aqueous medium.)

To optimise the temperature, this reaction was carried out at different temperatures and the results are consolidated in table 3. The temperature and the reaction time highly influenced the yield. Due to the formation of a small amount of homocoupling product, a long reaction period reduced the yield. The reaction afforded low yields when the temperature was raised to 60 °C because the high temperature reduced the solubility of  $\text{NH}_3$  in water.<sup>54</sup>

Table 3: Optimization of Temperature

Sl. No.	Temperature (°C)	Time (h)	Yield (%)
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1	Room Temperature	6	87
2	Room Temperature	9	96
3	Room Temperature	12	96
4	Room Temperature	24	90
5	40	10	96
6	40	12	96
7	50	10	91
8	60	10	85

(Reactions conducted with 3 mmol 4-bromoanisole, 10 mL of 0.5 M ammonia solution, 0.3 mol% PPECH-Amine-Cu catalyst, in water medium.)

Stirring of Aryl halides with ammonia solution for 9 h in aqueous medium at room temperature was fixed as the optimized condition for the synthesis of aryl amines. To analyze the generality of the reaction, this optimized protocol was applied for different aryl halides, and the results are tabulated in table 4.

**Table 4: Scope of the reaction**

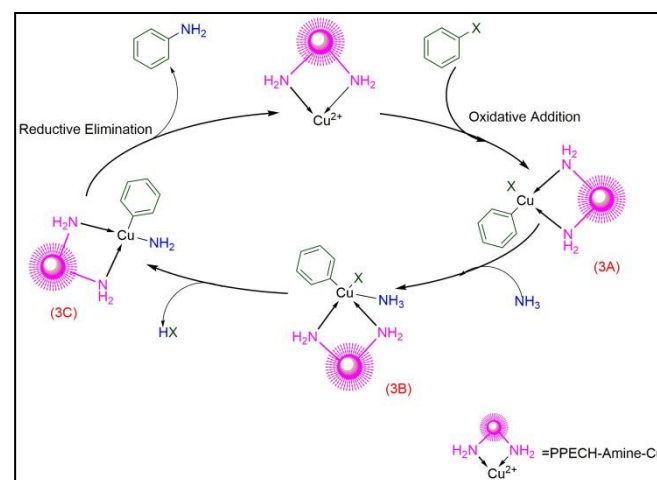
Sl. No.	Aryl halide	Time (h)	Yield (%)
1	4-Bromoanisole	9	96
2	2-Bromoanisole	9	94
3	2-Bromophenol	9	93
4	4-Bromophenol	9	94
5	Bromobenzene	9	95
6	Iodobenzene	9	96
7	4-Iodoanisole	9	97
8	2-Iodoanisole	9	95
9	2-Iodophenol	9	96
10	4-Iodophenol	9	95
11	1,2-Dibromobenzene	12	92
12	1,2-Diiodobenzene	9	94
13	2-Bromotoluene	9	92
14	4-Bromotoluene	9	93
15	2-Iodotoluene	9	93
16	4-Iodotoluene	9	94
17	1-Bromo-3-chlorobenzene	9	96
18	2-Bromo-4-nitrotoluene	9	97
19	2-Iodo-4-nitrotoluene	9	98
20	3-Bromobenzoic acid	9	97
21	3,5-Dibromobenzoic acid	9	92
22	1-Iodo-4-Nitrobenzene	9	98
23	4-Bromobiphenyl	9	96
24	4-Iodobiphenyl	9	97
25	1-Bromonaphthalene	9	95
26	1-Iodonaphthalene	9	97

(Reactions conducted with 3 mmol aryl halide, 10 mL of 0.5 M ammonia solution, 0.3 mol % PPECH-Amine-Cu catalyst, in water medium, room temperature, 9h.)

From this study, it can be inferred that the substituent of the haloarenes has a limited effect on the product yield. More specifically, the haloarenes bearing electron-withdrawing groups exhibited slight increase in activity than those having

electron-donating groups. For example, 1-Iodo-4-Nitrobenzene afforded a yield of 98% in contrast to 4-Iodotoluene for which only 93% of yield was observed under similar reaction conditions (Table 4, Entry 22 and 16). The presence of electron withdrawing group on the haloarenes improved the electrophilic nature, which promoted the amination reaction and resulted in higher yields. From the presented results, it could be seen that the PPECH-Amine-Cu catalyst efficiently catalyzed the amination of aryl halides with excellent yields in the absence of an external base, which was usually required to stimulate the amination reaction of aryl halides. The strong basic property of PPECH-Amine made the Cu complex more active, which triggered the better activation of the coordinated haloarenes towards the attack of ammonia.

#### Postulated mechanism



**Fig. 11: Proposed Mechanism**

From the previously reported works,<sup>55-57</sup> the above mechanism (Fig.11) was postulated. The oxidative addition of aryl halides to PPECH-Amine-Cu catalyst resulted in the formation of complex 3A. Addition of  $\text{NH}_3$  to this complex led to the formation of 3B, followed by the elimination of HX from 3B to 3C. The reductive elimination of 3C regenerated the PPECH-Amine-Cu catalyst and the formation of the product.

#### Leaching of Copper and Reusability study

Due to the good hydrophilic nature of the dendritic polymer-copper complex, it can easily be separated from the product by simple water wash. Since the molecular mass of the polymer-copper complex was high, it got settled down during the centrifugation by the application of rotation speed of 1800 rpm for 30 min.<sup>58,59</sup> Potential copper leaching from the complex into the reaction mixture was also investigated with ICP/OES analysis. For this purpose, the product was thoroughly washed with water. Centrifugation of washed water resulted in the settlement of pure catalyst. The metal content of the separated catalyst and the supernatant liquid were analyzed by ICP/OES. From the ICP analysis, it was found that the copper content in the supernatant liquid was less than 50 ppb and that of the recovered catalyst was 19.12 %.

Both findings revealed that practically no copper was leached from the catalyst. The recovered catalyst was reused up to six reaction cycles without loss of its activity (Fig.12). To explore more idea about the recyclability of the catalyst, experiments were conducted and 0.15 mole% was optimized which was the lowest quantity of catalyst to make the 50 % conversion of substrates. The catalyst was reused up to 20 reaction cycles in which the 50 % yield was changed to 40 %.

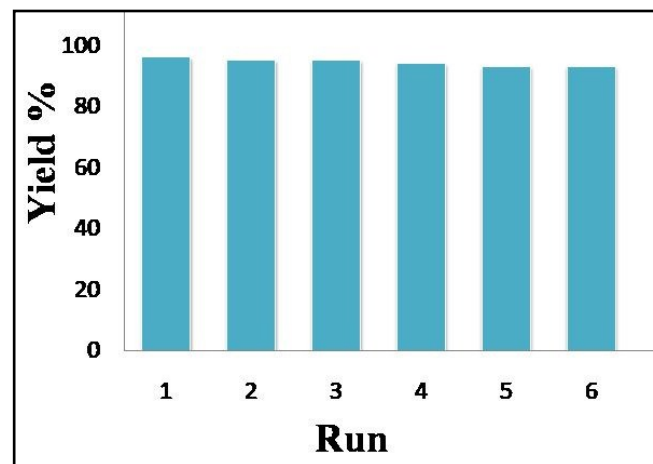


Fig. 12: Reusability of PPECH-Amine-Cu catalyst

#### Comparison study with previously reported Catalysts

Table 5: Comparative study

S. I. No	Catalyst	T (°C)	Time (h)	Solvent	Base	Yield (%)	Ref
1	Fe <sub>2</sub> O <sub>3</sub> -CuI	90	16	Ethanol	NaOH	85	60
2	N <sup>2</sup> , N <sup>2</sup> -Diisopropylalohydrazide Copper complex	60	24	H <sub>2</sub> O	K <sub>3</sub> PO <sub>4</sub>	89	35
3	CuI, L-proline 40 mol%	R. T	24	DMSO	K <sub>2</sub> CO <sub>3</sub>	97	61
4	(Cu(acac) <sub>2</sub> )	90	24	DMSO	CS <sub>2</sub> CO <sub>3</sub>	92	62
5	CuOAc, NaOAc	100	12	DMSO	NMO	92	63
6	PPECH-Amine-Cu	R. T	9	H <sub>2</sub> O	-	96	This work

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## Conclusions

A porphyrin cored amine functionalized dendritic polymer and its copper complex (PPECH-Amine-Cu) was effectively synthesized. The PPECH-Amine-Cu catalyst was highly active and selective for the coupling of ammonia with aryl bromides and iodides to form primary arylamine products. Due to the presence of numerous free amino groups in PPECH-Amine-Cu, this method did not require any extra base additives which was essential for most of the previously reported amination reactions. So this catalyst system has the scope to include reactions of certain aryl halides containing base-sensitive functional groups, such as carboxylic acid. Reusability, solubility and high activity of the catalyst even at room temperature, fashioned it as an eco-friendly green catalyst.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

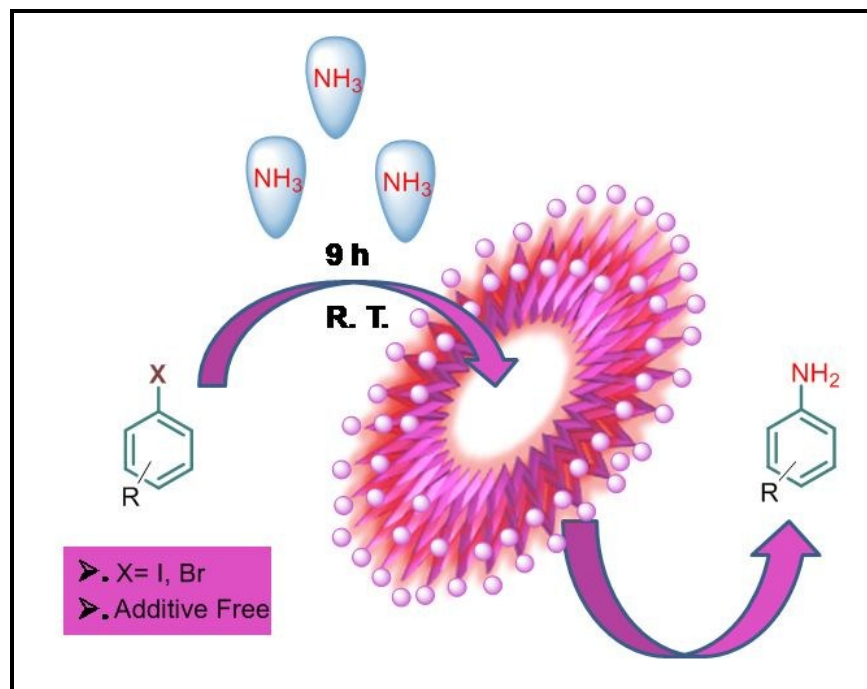
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Additive free synthesis of aryl amines from aryl halides using reusable water soluble porphyrin cored amine functionalized dendritic polymer copper complex (PPECH-Amine-Cu) catalyst in aqueous media.