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Integrating CuO-Fe₂O₃ Nanocomposites and Supramolecular Assemblies of Phenazine for Visible Light Photoredox Catalysis

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Abstract: Photoredox catalytic ensemble consisting of CuO-Fe₂O₃ nanocomposites and oligomeric derivative of phenazine has been developed. The prepared system acts as an efficient photoredox catalyst for C-N bond formation reaction *via* SET mechanism under 'green' conditions (aerial environment, mixed aqueous media, recyclable) requiring less equivalents of base and amine substrate. The present study demonstrates the significant role of supramolecular assemblies as photooxidants and reductants upon irradiation and their important contribution towards the activation of the metallic centre through energy transfer and electron transfer pathways. The potential of oligomer **4**: CuO-Fe₂O₃ has also been explored for C-C bond formation reactions *via* Sonogashira protocol.

Introduction

The formation of carbon-carbon and carbon-heteroatom bonds via palladium-catalyzed coupling reaction is an outstanding tool for the preparation of pharmaceutically active compounds and functional materials.¹⁻⁴ Though the palladium-based catalytic systems are efficient but the toxic nature of palladium is a big hurdle towards the development of sustainable synthetic approaches. Besides its toxic nature, high cost and sensitive handling of the palladium complexes⁵ encouraged the organic chemists to develop easy to handle and relatively economical copper-based catalytic systems.⁶ Despite the huge economical and environmental advantages of copper-based catalytic systems, some of the elements of reaction protocols such as the requirement of high temperature, additional ligands, a stoichiometric amount of metal reagents and strong bases remained unaddressed which need great attention to achieve 'green' organic transformations.⁷⁻⁹ To overcome the problems associated with thermal heating, a variety of photocatalysts comprising of economical and benign Ni complexes and photoactive ligands have been reported^{10,11} (Scheme S1). Most of the reported systems act efficiently in the presence of organic solvents and under inert conditions. Recently, from our lab, we reported a photocatalytic system based on nanocomposites (Cu₂O-Fe₂O₃) using assemblies of hexaphenylbenzene based derivative (Scheme S2), ¹² which could overcome the need for the thermal heating but the reaction protocol still needed high amount of amine as substrate (5.0 equiv.) and base (2.5 equiv.) to achieve product in higher yield. Excess substrate amine/base is generally needed in C-N coupling reactions for activation of the metallic center for generation of intermediates i.e. amino

radical and aryl radical. We hypothesized that by developing a photoredox catalytic ensemble which could act as photooxidants in an excited state and reductants at ground, the need for excessive amine substrate/base can be controlled. Thus, we planned to develop a catalytic system consisting of photoredox supramolecular assemblies and metallic center. For the recyclable metallic center, we focused on the development of nanocomposites consisting of copper and iron metallic species. Further, we planned to stabilize the nanocomposites using supramolecular assemblies which besides acting as lightharvesting antenna should also have the potential to serve as reductants at ground state and oxidants at excited state. Hence, we focused on synthesizing donor-acceptor platform (D-A) as such systems are known to show good redox potential and strong absorption in the visible region. Since the HPB derivatives show maximum absorption in the range of 300-350 nm¹¹, we planned to substitute HPB scaffold with dibenzo [a, c] phenazine (DBPZ) scaffold which is known for high absorption in the visible region.¹³ Furthermore, we incorporated donor amino groups at the periphery in the designed molecule 3 (DBPZNH₂) due to their known affinity toward soft metal ions such as copper. Interestingly, DBPZNH₂ formed fluorescent aggregates in mixed aqueous media which showed high affinity towards Cu²⁺ and Fe³⁺ ions and serve as reactors for reducing these metal ions simultaneously to furnish nanocomposites. During the reduction of metal ions, the assemblies of derivative DBPZNH2 are oxidized to generate oligomeric species 4 which show high absorption in the visible region, good photostability, low band gap and high redox potential in the ground state as well as in the excited state (vide infra). The approach being presented in this manuscript for preparation of CuO-Fe₂O₃ nanocomposites is rapid, economic and 'green' in comparison to the other reported approaches (Table S1). The supramolecular ensemble consisting of oligomeric species 4 and CuO-Fe₂O₃ nanocomposites showed high efficiency in C-N bond formation reactions. To our pleasure, the target product was achieved in 92% yield (Scheme 3, entry vii). Various control experiments confirm the contribution of supramolecular assemblies in the catalytic efficiency through electron/energy transfer processes. Interestingly, the need of high equivalents of amine substrate and base could be controlled under optimized conditions. The as prepared supramolecular ensemble presents a good example of supramolecular catalysis as each component of the ensemble is contributing towards the high catalytic activity of the system. Furthermore, the catalytic system also work efficiently in the C-C

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bond formation reaction via Sonogashira coupling in the presence of visible light, mixed aqueous media and under aerial conditions. The catalytic system could be recycled for four cycles without any change in the yield for C-C/C-N coupling reactions. To the best of our knowledge, this is the first report highlighting the contribution of supramolecular assemblies in enhancing the catalytic efficiency of the nanocomposites. In comparison to other reported systems, the catalytic system being presented in this manuscript could catalyze C-N as well as C-C bond formation reactions more efficiently (Table S2 and S3).

Results and Discussion

The Suzuki Miyaura coupling between 11, 12-dibromodibenzo [a,c] phenazine¹⁴ **1** and boronic ester of aniline¹⁵ **2** furnished the



Scheme 1. Synthesis of derivative 3 DBPZNH₂

yellow colored compound **3** named as $DBPZNH_2$ in 80% yield (Scheme 1). The structure of compound $DBPZNH_2$ has been characterized by various spectroscopic and analytical techniques (Figure S63-S66).

The UV-vis spectrum of DBPZNH₂ in THF exhibits absorption bands at 305 nm due to π - π * transitions of phenazine moiety and at 440 nm attributed to intramolecular charge transfer (ICT) state (Figure S1). Upon increasing the water fraction (10% to 99%) in the THF solution, a red shift of 15 nm was observed in the absorption band at 440 nm which suggests the formation of J- aggregates (Figure S2). The fluorescence spectrum of $\ensuremath{\text{DBPZNH}}_2$ in THF exhibits dual emission bands at 430 nm attributed to locally excited state (LE) and at 580 nm attributed to twisted intramolecular charge transfer (TICT) state. A large Stokes shift in solvent dependent studies and enhancement in the emission intensity of the band at 580 nm with a blue shift on increasing the temperature confirms the presence of the TICT state¹⁵ (Figure S3 and S4). The fluorescence spectra of DBPZNH₂ in mixed aqueous media and viscosity dependent studies indicate the aggregation-induced emission characteristics of the molecule (Figure S5 and S6). The transmission electron microscopic (TEM) image of DBPZNH2 in H₂O/THF (5/5) solvent mixture show the presence of spherical shaped aggregates (Figure S7). Further, the dynamic light scattering studies (DLS) indicate that the average size of aggregates is in the range of 200-500 nm (Figure S8).

Next, we evaluated the binding affinity of assemblies of **DBPZNH**₂ toward various metal ions such as Zn²⁺, Cu²⁺, Hg²⁺, Fe²⁺, Fe³⁺, Co²⁺, Pb²⁺, Pd²⁺, Ni²⁺, Cd²⁺, Ba²⁺, Mg²⁺, Ag⁺, and Al³⁺ by UV- vis spectroscopy. Upon gradual addition of Cu²⁺ ions (0-50 equiv.) to the solution of **DBPZNH**₂ (5 μ M) in H₂O/THF (5/5, v/v) solvent mixture, a new band is observed at 720 nm with the

gradual increase in intensity with time (30 min) (Figure S9). These spectral changes are accompanied by the color change of the solution from light yellow to brown which indicates the formation of CuO NPs. Further, upon addition of Fe³⁺ ions (0-30 equiv.) to the solution of DBPZNH₂ (5µM) in H₂O/THF (5/5, v/v) solvent mixture, a broad band appeared around 550 nm which is attributed to SPR band of Fe₂O₃ nanoparticles (Figure S10). A visible color change from light yellow to intense yellow was observed to the naked eye. These studies indicate the potential of assemblies of DBPZNH₂ for the preparation of CuO and Fe₂O₃ NPs.^{12, 15} Under the same conditions as used above for Cu²⁺ and Fe³⁺ ions, we also tested the UV-vis and fluorescence response of assemblies of DBPZNH₂ toward other metal ions such as (Fe²⁺, Co²⁺, Pb²⁺, Zn²⁺, Ni²⁺, Pd²⁺, Ag⁺, Hg²⁺ ,and Mg²⁺) as their chloride salts but no significant change in the absorbance behavior was observed in the presence of these metal ions (Figure S11).



Figure 1. (a) UV-vis spectra of derivative **DBPZNH**₂ upon addition of Cu²⁺ and Fe³⁺ ions simultaneously in H₂O/THF (5/5) mixture. (b) Visible colour change upon addition of Cu²⁺ and Fe³⁺ in the solution of **DBPZNH**₂ derivative.

Having established, the potential of the assemblies of **DBPZNH**₂ to generate CuO and Fe₂O₃ NPs, we prepared nanocomposites of CuO–Fe₂O₃ using the supramolecular assemblies of **DBPZNH**₂ as a common platform. We simultaneously added the solution of Cu²⁺ ions (0-50 equiv.) and Fe³⁺ions (0-30 equiv.) to the solution of **DBPZNH**₂ in H₂O/THF (5/5, v/v) solvent mixture and kept the solution for 30 min at room temperature. The absorption spectrum of the above solution shows absorption bands at 550 nm and 750 nm with the visible color change of the solution from light yellow to dark brown (Figure 1). These spectral changes indicate that assemblies of **DBPZNH**₂ could simultaneously reduce both ions to generate CuO–Fe₂O₃ nanocomposites.^{12, 15}

To shed more light on the mechanistic pathway for the formation of metal nanoparticles using supramolecular assemblies of **DBPZNH**₂, we examined the interactions between assemblies of **DBPZNH**₂ and Cu(II)/Fe(III) ions under inert and aerial atmosphere. For this, we added Cu(II) ions to the assemblies of the **DBPZNH**₂ and stirred the solution under the inert atmosphere. After 20 minutes, a small portion of the solution was withdrawn and its absorption spectrum was recorded which shows the formation of a new band at 555 nm corresponding to

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Cu(0) species.¹⁵ When the solution was left under aerial conditions for half an hour, the band at 555 nm disappeared and a new band appeared at 720 nm corresponding to CuO NPs (Figure S12). A similar experiment was carried out with Fe (III) ions under inert and aerial conditions. Initially, the bands at 263 and 350 nm corresponding to Fe(0) species (Figure S13),^{16,17} were observed which upon exposure to aerial conditions disappeared and a new band corresponding to Fe₂O₃ NPs appears at 550 nm. These results clearly show that initially Cu(0)/Fe(0) NPs are produced and air oxidation leads to the formation of respective metal oxide NPs i.e. CuO and Fe₂O₃.

The TEM image of supramolecular assemblies of **DBPZNH**₂ in mixed aqueous media in the presence of Cu²⁺ and Fe³⁺ ions show the presence of spherical shaped nanocomposites supported over oxidized species (Figure 2). The DLS studies confirm the average size of nanoparticles in the range of 30–50 nm in the H₂O/THF (5/5) solvent mixture (Figure S14). From thermogravimetric analysis (TGA), the organic part was found to be 16% by weight in the supramolecular ensemble (Figure S15). The inductively coupled plasma- optical emission spectrometry (ICP-OES) studies showed the presence of 44.5 wt % of copper and 22.5 wt % of the iron in the CuO-Fe₂O₃ nanocomposites (Figure S16). The X-ray diffraction peaks of precipitates



Figure 2. (a) TEM image of CuO-Fe₂O₃ NPs supported over organic part (scale bar 500 nm). (b) TEM image of CuO-Fe₂O₃ nanocomposites formed by using $DBPZNH_2$ (scale bar 100 nm).

obtained by evaporating THF/H₂O solution of DBPZNH₂, CuCl₂ and FeCl₃) at 23.98, 33.06, 35.48, 38.62, 48.36, 53.88, 57.44, 61.22, 63.86, 65.80, 67.84, 72.06 and 74.74 support the formation of CuO and Fe₂O₃ NPs (Figure S17).¹⁸ The highresolution XPS spectrum shows binding energy peaks at 933 and 953 eV corresponding to Cu 2p3/2 and Cu 2p1/2 spin-orbital components confirmed the formation of CuO nanocomposites, respectively. Further, the binding energies peaks at 712 and 723 eV corresponding to Fe $2p_{1/2}$ and Fe $2p_{3/2}$ indicate the formation of Fe_2O_3 nanocomposites (Figure S18).^{15,19} The FT-IR studies show bands corresponding to Cu-O and Fe-O stretching at 462 cm⁻¹ and 536 cm⁻¹, respectively, (Figure S19) which suggests the formation of the CuO-Fe₂O₃ nanoparticles.^{12,15} The magnetic hysteresis measurement of the same material shows the superparamagnetic nature of generated CuO-Fe₂O₃ nanocomposites (Figure S20).¹²

To elucidate the structure of oxidized species, we slowly evaporated the solution of **DBPZNH**₂ containing CuCl₂ and FeCl₃. After 2 days, precipitates were formed which were filtered and washed with organic solvents (THF/CHCl₃). The ¹H NMR

spectrum of the residue obtained after evaporating the solvent shows the broadening of the aromatic protons with the appearance of additional peaks at 6.9 and 7.5 ppm which indicates the oxidation of DBPZNH2¹⁵ (Figure S21). Further, the GPC analysis of the sample corroborates the oxidation of DBPZNH₂ leading to the formation of oligomeric oxidized species 4 (Figure S22). The DLS experiment indicates the size of aggregates of oligomeric species in the range of 300- 600 nm (Figure S23). The powder XRD analysis of oxidized species shows a broad peak at $2\Theta=25^{\circ}$ corresponding to the characteristic peak of polyanilines²⁰ (Figure S24). The FT-IR spectrum shows a broad stretching band at 3500 cm⁻¹ corresponding to primary and secondary amines in the oligomeric species 4 of DBPZNH2¹⁵ (Figure S25). We believe that upon reduction of metal ions the DBPZNH₂ itself undergoes oxidation to form oligomeric species 4 (Scheme 2).



Scheme 2. Possible schematic representation of formation of CuO-Fe₂O₃ nanocomposites by using DBPZNH₂ in mixed aqueous medium.

Next, we examined the photophysical properties of oligomeric species 4 in THF/H₂O solvent mixture. The oligomeric species 4 absorbs strongly in the visible region with maxima at 400 nm (Figure S26). Further, we checked the photostability of oxidized species, by exposing the solution of oligomeric species 4 in mixed aqueous media to visible light irradiation for 6 h. To our pleasure, only a slight change in the absorption properties was observed which indicates high photostability of oxidized species 4 (Figure S27). The fluorescence spectrum of the oxidized species 4 in mixed aqueous medium shows an emission band at 500 nm. Interestingly, upon the addition of bare CuO-Fe₂O₃ nanocomposites $^{21,\,22}$ to the solution of oligomeric species $\boldsymbol{4},\,60\%$ quenching of the emission was observed (Figure S28). Further good spectral overlap was observed between the emission of oligomeric species 4 and the absorption spectrum of hybrid metal nanocomposites (Figure S29). These results indicate the possibility of energy transfer from oligomeric species 4 to nanocomposites. From cyclic voltammetry studies, the reduction potential of oligomeric species 4 was found to be -1.6 V and the HOMO-LUMO gap was calculated to be 2.48 eV (Figure S30). The excited state reduction potential as calculated by the Rehm Weller equation was found to be +1.00 V. These studies indicate the potential of oligomeric species 4 to act as photooxidant in excited state and photoreductant in the ground state. To confirm the possibility of electron transfer from amine substrate to assemblies, we examined the emission behavior of oxidized species in the presence of morpholine (Figure S31). To our

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delight, the emission spectra was fully quenched, which confirms the potential of assemblies to act as photooxidant in the presence of morpholine substrate as donor.²³

The strong absorption of the supramolecular ensemble in the visible region with sufficient redox potential (ground as well as excited state) and good photostability of oligomeric species 4 motivated us to explore the photocatalytic efficiency of the supramolecular ensemble of oligomer4@CuO-Fe₂O₃ nanocomposites in C-N cross coupling reaction under visible light irradiation. We chose a reaction between 1-iodobenzene (1 equiv.) and morpholine (5 equiv.) in the glycerol/ H_2O (5/5) solvent mixture as the model reaction in the presence of supramolecular ensemble of oligomer4@CuO-Fe₂O₃ nanocomposites (0.5 mol%) as photoredox catalyst under aerial conditions (Scheme S3). To our pleasure, the reaction was complete in 4 h to furnish the product in 92% yield (Table S4, Entry 1). The TON and TOF values were found to be 18.4, 4.6 which shows the high activity of the catalytic system (Table S5). Next, the model reaction was repeated in different solvents such as glycerol, ethanol, DMF, DMSO, and water (Table S4, Entries 2-6). The desired product was obtained in comparable vields in case of glycerol, glycerol/ H₂O (5/5) and ethanol. We chose alvcerol/H₂O (5/5) mixture as the reaction medium for carrying out further reactions (Table S4, Entry 1). Further, the effect of switching of the base was investigated on the photocatalytic C-N cross coupling reaction (Table S4, Entries 7, 8). Interestingly, no significant change in the model reaction was observed by switching the base. We chose K₂CO₃ as the base for further investigation due to easy accessibility. To optimize the amount of base required for coupling reactions, we carried out the model reaction by reducing the amount of base from 2.5 equiv. to 1.0 equiv. The product was obtained in almost same yield but



Scheme 3. Schematic illustrations of C-N cross coupling using CuO NPs, Fe_2O_3 NPs, and oligomeric species 4 separately as photocatalyst.

time increased from 4 to 7 hours (Table S4, Entry 9). But in the absence of base desired product was obtained only in trace amount which suggests that basic media is indispensable for carrying out coupling reaction (Table S4, Entry 10). Next, we repeated the model reaction using a lower amount of morpholine (from 5.0 equiv. to 3.0 equiv.) under optimized conditions and the desired product was obtained in 90% yield (Table S4, Entry 11). Upon further reducing the amount of morpholine from 3.0 equiv. to 2.0 equiv., the yield decreased to 65% (Table S4, Entry

12). The model reaction was also carried under dark conditions to understand the importance of visible light, however, the desired product was obtained only in traces which supports the role of visible light in the reaction (Table S4, Entry 13). In the next part of the investigation, we carried out various control experiments to examine the role of each component of the supramolecular ensemble (Scheme 3). The model reaction was independently carried out in the presence of bare nanoparticles, in case of CuO NPs²¹ the yield of the final product was found to be 30% (Scheme 3, entry i) and with Fe₂O₃ NPs²² product was obtained in 25% yield in 12 h (Scheme 3, entry ii). We also carried out the reaction in the presence of oligomeric species 4 but the yield of the desired product was found to be 25% (Scheme 3, entry iv). Although the target product is furnished in low yield but these studies indicate the capacity of each





component of an ensemble to carry out reactions in the isolated state. We observed an increase in the yield of the desired product upon taking the NPs and oxidized species together. However, the reaction did not proceed in the absence of a catalytic system under optimized conditions (Scheme 3, entry viii).

After optimizing the reaction conditions, we investigated the substrate scope with regards to amines and aryl halides. Secondary and cyclic amines like pyrrolidine and piperidine were also examined as coupling partners (Scheme 4).

We also examined several reactions by changing the amines from aniline and diphenylamine with aryl halides under optimized conditions. Interestingly, in all the cases target compounds were obtained in excellent yields (Scheme S4).

Heterocyclic amines were also examined as substrates and all the tested amines furnished the desired products in good to excellent yields (Scheme 5). Interestingly, in all the reactions no column chromatography was needed for the purification of the

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products except derivatives 11a, 12a. The TONs and TOFs of all the desired products has been determined and these values shows the high efficiency of the catalytic system in catalyzing C-N cross coupling reactions (Table S5).

Further, to investigate the reaction mechanism of C-N coupling reactions catalyzed by oligomer4@CuO-Fe₂O₃ nanocomposites, we carried out the model reaction in the presence of radical scavenger 2, 2, 6, 6-tetramethyl-1-piperidinoxyl (TEMPO)¹¹ (Scheme 6a). The yield of the desired product was drastically decreased and the formation of the adduct of 4-iodobenzene and TEMPO was detected (Figure S32). This result indicates that the reaction proceeds through a single electron transfer pathway (SET). Furthermore, the outcome of control reactions



Scheme 5. The C–N coupling reaction between substituted aryl halides and heterocyclic amines in H_2O /glycerol (5/5), using oligomer4@CuO-Fe₂O₃ NPs under visible light irradiation.

between an aryl halide and morpholine (3.0 equiv.) (Table S4, Entry 11, 12) clearly shows that at least 3.0 equivalents of amine substrate are required for a complete transformation at a faster rate. Thus, substrate amine is contributing towards the enhancement of catalytic activity. Further, in the FT-IR spectra of the reaction mixture of morpholine and iodobenzene in the presence of oligomer4@CuO-Fe₂O₃ NPs, no peak at 3295 cm⁻¹ (corresponding to N-H of morpholine) was observed²⁴ (Figure S33). Based upon all the experimental results, we believe that upon visible light irradiation, the supramolecular assemblies interact with amine and accept the electron from amine in the excited state. Since the energy of the conduction band of CuO NPs is lower than that of LUMO of the assemblies, the transfer of electrons from LUMO of assemblies to the conduction band of NPs is favored. As a result of which electron density is increased on the surface of metallic species (Scheme 6b)²⁴ for activation of C-X bond and N-H bond which results in the formation of the final product. Thus, supramolecular assemblies of oligomeric species 4 are assisting the metallic center via energy transfer and electron transfer processes for carrying out C-N cross coupling reaction (Scheme 6c).1

Further, we chose a reaction between 1-iodobenzene and morpholine as a model reaction to determine the recyclability of the *in-situ* generated supramolecular ensemble of oligomer4@CuO-Fe₂O₃ nanocomposites as the catalyst. The CuO-Fe₂O₃ nanocomposites could be easily separated from the reaction mixture due to their magnetic nature and were recycled in the next round of the model reaction (Figure S34). The yield of the desired product remained almost same in the four cycles. The TEM image of the recovered catalyst after 3rd cycle show

no significant change in the morphology (Figure S35 a), however, the TEM image of the recovered catalyst after the 4th cycle shows slight change in the morphology (Figure S35 b). After the fourth cycle, the yield reduced to 75% (Figure S36) which was due to slight change in the PXRD of recovered catalyst (Figure S37) and leaching of 1.006 ppm of copper in residual solvent confirmed by atomic absorption spectroscopy(AAS) (Figure S38).

Encouraged by the above findings which demonstrate high efficiency of as prepared catalytic ensemble in C-N bond formation reactions, we examined the efficiency of the supramolecular ensemble of oligomer4@CuO-Fe₂O₃ nanocomposites in C-C bond formation reactions via Sonogashira protocol. The reaction between 1-iodobenzene and phenylacetylene was chosen as a model reaction. The model reaction was carried out under optimized conditions of C-N



Scheme 6. (a) The model reaction in the presence of TEMPO as radical scavenger. (b) Schematic representation for energy transfer and electron transfer by supramolecular assemblies of oligomeric species **4.** (c) The proposed mechanism for C-N coupling catalysed by oligomer**4**@CuO-Fe₂O₃ NPs as photocatalyst under visible light irradiation.

coupling. As expected, the desired product was obtained in 85% yield after 4 h (Scheme S5 entries viii). In literature, costly metal-

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based complexes (such as gold and palladium) have been utilized as photocatalysts for carrying out Sonogashira coupling.²⁶ Recently, TiO₂ as photocatalyst in combination with CuO NPs has also been reported as photocatalyst for carrying out Sonogashira reaction (Scheme S6).27 Besides the cost of photocatalyst, the reaction conditions required the presence of additional bases and inert atmosphere. In comparison, oligomer4@CuO-Fe2O3 nanocomposites furnished the desired product in excellent yield under aerial conditions using K₂CO₃ as the base. Next, we carried several experiments to examine the role of each component (CuO NPs, Fe₂O₃ NPs and assembly) in the reaction (Scheme S5 entries i, ii, iv). These studies show that CuO and Fe₂O₃ NPs in combination with oxidized species 4 could catalyze Sonogashira reaction more efficiently. These studies reveal relatively less contribution of supramolecular assemblies in catalyzing the C-C bond formation reactions. We believe that due to the absence of activating stimulus (electronrich amine as the donor) the potential of assemblies to activate C-X bond is decreased. To confirm this assumption, we repeated the model reaction using oligomeric assemblies 4 and



Scheme 7. The Sonogashira coupling reaction between substituted aryl halides and phenylacetylene in H₂O/Glycerol (5/5) utilizing oligomer4@CuO-Fe₂O₃ nanocomposites as photocatalyst under visible light irradiation.

triethylamine as the base. The target product was achieved in 20% yield and in presence of *in situ* generated oligomer4@CuO-Fe₂O₃ nanocomposites the target product was furnished in 92%. These findings support our assumption regarding the activation of assemblies by donor substrate amine (Scheme S5 entries v and ix).

With these optimized conditions in hand, we checked the substrate scope with regard to different aryl halides. The Sonogashira reaction was examined using aryl halides having bromo and chloro as the leaving group and phenylacetylene using supramolecular ensemble of oligomer4@CuO-Fe₂O₃ nanocomposites as photocatalyst. Interestingly, reactions with bromobenzene and chlorobenzene went smoothly to furnish the desired products in good yield (Scheme S7).

Further, we checked the scope with substituted aryl halides having electron-withdrawing as well as electron-donating groups. All the substrates furnished target products in good to excellent yields (Scheme 7). All the products were purified by recrystallization from the organic solvents. The TONs and TOFs of the desired products had also been calculated which show the high efficiency of the catalyst for carrying out C-C coupling reactions (Table S6).

To get insight into the reaction mechanism, we carried out the reaction in the presence of TEMPO (Scheme 8a). We were

Further, to understand the activation of acetylene²⁸, we recorded the FTIR of the phenylacetylene and reaction mixture of a model reaction containing the reactants (iodobenzene and phenylacetylene) and catalytic system. The FT-IR spectrum of the reaction mixture showed no peak at 3287 cm⁻¹ corresponding to acetylenic hydrogen (Figure S40). On the basis of the above experiments and literature reports, we proposed the mechanism for C-C coupling reaction. We believe that upon irradiation of light, the oligomer4@CuO-Fe2O3 activates C-H bond of alkyne and metal acetylide complex (A*) is generated which acts as a photocatalyst. Simultaneously the catalytic system generates any radical which finally interacts with metal acetylide leading to formation of the desired alkynylated product (Scheme 8b).





Scheme 8. (a) The model reaction in the presence of TEMPO. (b) The proposed mechanism for Sonogashira coupling catalyzed by oligomer4@CuO-Fe₂O₃ nanocomposites as photocatalyst under visible light irradiation.

We also checked the recyclability of the system for C-C coupling reaction. The catalytic activity remained unchanged for four cycles. After the 4th cycle, a slight decrease in the yield of the desired product was observed (Figure S41).

Conclusion

In conclusion, the integration of CuO-Fe₂O₃ nanocomposites and assemblies of oligomeric species **4** led to the development of a highly efficient recyclable photoredox catalytic system for C-

N/C-C coupling reaction under green conditions. The reactions proceed through the SET mechanism and oligomeric species **4** contribute significantly towards the activation of nanocomposites through electron/energy transfer processes. The catalytic cycle could be recycled for four cycles without any loss in the yield of the target compound in model reaction. All the target compounds could be purified by recrystallization and no column chromatography was needed.

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Keywords: Photoredox system • CuO-Fe₂O₃ Nanocomposites • Supramolecular assemblies • C-N coupling • Sonogashira coupling

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The supramolecular assemblies of **DBPZNH**₂ act as a nanoreactor for the formation of CuO-Fe₂O₃ NPs in aqueous media at room temperature. Further, the supramolecular ensemble catalyses C-C and C-N couplings under mild conditions such as aerial atmosphere, mixed aqueous media, visible light. The as-prepared supramolecular ensemble presents a good example of supramolecular catalysis as each component of the ensemble is contributing towards the high catalytic activity of the system. The system also illustrates the potential of oligomeric species to harvest visible radiations as well as generate the activated species for the formation of C-N bond in the isolated state.