Journal of Catalysis 401 (2021) 297-308

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Surface engineered Iridium-based magnetic photocatalyst paving a path towards visible light driven C-H arylation and cyanation reaction



JOURNAL OF CATALYSIS

Pooja Rana^a, Rashmi Gaur^a, Bhawna Kaushik^a, Pooja Rana^a, Sneha Yadav^a, Priya Yadav^a, Priti Sharma^c, Manoj B. Gawande^{b,*}, Rakesh K. Sharma^{a,*}

^a Green Chemistry Network Centre, Department of Chemistry, University of Delhi, New Delhi 110007, India

^b Department of Chemistry and Engineering, Institute of Chemical Technology Mumbai-Marathwada Campus, Jalna 431213, Maharashtra, India

^c Regional Centre of Advanced Technologies and Materials, Czech Advanced Technology and Research Institute, Palacký University, 779 00 Olomouc, Czech Republic

ARTICLE INFO

Article history: Received 8 April 2021 Revised 10 July 2021 Accepted 2 August 2021 Available online 9 August 2021

Keywords: Photoredox Nanocatalyst Magnetically retrievable Visible light Heterogeneous catalyst

ABSTRACT

The report presents the fabrication and application of a highly versatile, magnetic and robust iridium based photoredox nanocatalyst. Herein, Ir(PPy)₃ based photocatalyst sites have been chemically engineered over the magnetic nanoparticles to encompass the captivating features of homogeneous iridium photocatalyst with the magnetically recyclable core. A household photoreactor was designed and fabricated to achieve highly selective visible light driven oxidative C-H arylation and C-H cyanation under sustainable and ambient reaction conditions utilizing the Ir@PyBz@ASMNPs photoredox nanocatalyst. The environment friendly Ir@PyBz@ASMNPs shows excellent photocatalytic activity, broad substrate adaptability and outstanding recyclability compared to the analogous homogeneous catalysts. Indeed, the Ir@PyBz@ASMNPs possess some key features including high surface area, high iridium metal loading and excellent stability. This work is expected to enlighten and provide new insights in the rational design of high performance and recoverable photoredox nanocatalyst through surface engineering strategy.

© 2021 Elsevier Inc. All rights reserved.

1. Introduction

Photoredox catalysis has gained colossal attention for engineering environmentally sustainable processes due to its ability to exploit inexpensive, clean and endless renewable solar energy to engage single electron transfer (SET) for synthetic manipulation or catalytic activation of organic molecules [1]. Over the past few years, numerous research groups have widely employed the power of light for various applications such as photocatalysis, photodegradation, singlet oxygen generation, water splitting, reduction of carbon dioxide, etc. [2-5]. In fact, several transition metals based homogeneous catalysts (such as ruthenium, iridium and copper polypyridyl complexes) and organic moieties (like eosin Y, rose bengal etc.) have garnered particular appreciation in the field of photocatalysis [3,6–9]. These photocatalysts possess various attention grabbing properties such as energy efficiency, stability, absorbance in visible range, long-lived photoexcited states, versatile nature and readily tunable photophysical properties by modification of the ligand scaffold [6]. Unlike the thermal

* Corresponding authors. *E-mail addresses:* mb.gawande@marj.ictmumbai.edu.in (M.B. Gawande), rksharmagreenchem@hotmail.com (R.K. Sharma). and UV light catalyzed reactions, the visible light catalyzed reactions reduce the possibility of side reactions due to lack of visible light absorbance by organic compounds [9,10].

Over the years, the chemistry of tris-cyclometalated coordinatively saturated, 18-electron d⁶ complexes of iridium, such as Ir $(ppy)_3$, has been the focus of great attention due to the ease of synthesis and diversification, stability at room temperature, and excellent photoredox properties [11,12]. Additionally, the iridium complexes unveil a wide variety of applications in the field of solar cells, light-emitting diodes (LEDs), sensing, biology and as initiators in free radical polymerization [12]. Despite these abovementioned advantages, progress must be made toward ease of separation, recyclability, stability, and environmental neutrality of these photoredox catalysts in order to move the field toward practical utility in academia and industry [13,14]. Consequently, the development of a heterogeneously immobilized photosensitizer system that maintains photoredox capability upon immobilization is a significant step toward this goal. Henceforth, coordination chemistry delivers a new pathway for engineering heterogeneous supports through immobilizing photocatalytically active sites having high activity and selectivity. To date, a limited number of covalently or physically immobilized photoredox catalyst over cores (such as graphene, TiO₂, silica, polymer, ZnO, NPs etc.) have been



developed and utilized for catalytic applications [15–19]. Apart from their countless advantages and tremendous efforts in the field, certain drawbacks such as difficult surface modification to introduce chelating sites, durability, reduced recyclability and serious economic and environmental issues need to be resolved. Hence, a versatile heterogeneous system is required which can overcome these aforementioned challenges and can be further explored for efficient organic transformation of pharmaceutically viable motifs (such as biaryls, α -aminonitriles etc.) in the presence of visible light.

Biaryl moieties are ubiquitous and are utilized extensively in a variety of materials, catalytic systems, biological and pharmaceutical fields. The biaryl motifs also show high utility in various molecular switches, motors and medicines such as antibiotic, angiotensin receptor blockers (ARBs), antifungal, anticancer, anti-inflamma tory/antiarthritic, analgesic, antiemetic as well as antihypertensive drugs (Fig. 1) [20–22]. Despite various achievements in the field, the C-C bond formation reaction by availing various transition

metals remain the center of attraction among the scientific community [23–25]. However, the previously reported methodologies have several limitations such as utilization of highly toxic and unrecoverable catalysts, harsh reaction conditions like bulk amount (more than 3 equiv.) of strong base, longer reaction time, and elevated temperatures [26-28]. On a different note, researchers have also explored straightforward approaches for the C-C bond formation by utilizing AgF based and nickel superstructure heterogeneous photocatalysts for the synthesis of biaryls (see comparison table S1a). Unfortunately, the involvement of high power consuming white light sources (such as Xenon lamps with power more than 100 W) as well as destructive nature of UV radiation, rigorously dry conditions, and low recyclability limits the largescale efficacy (see comparison table S1a). Recently, our group devised a magnetically retrievable ruthenium based photocatalytic system. Ru@DAFO@ASMNPs, which exhibited outstanding catalvtic performance [29]. In extension to our ongoing research work. [30-33] our efforts are to design and develop a heterogeneous pho-



toredox nanocatalyst by adopting the coordination chemistry for stably anchoring the iridium metal complex over the magnetic support to achieve a highly efficient, robust, cost-effective, magnetically retrievable and reusable system.

Henceforth, Scheme 1 was employed to acquire the iridium based magnetically retrievable photoredox nanocatalyst. Initially, the magnetic nanoparticles of Fe₃O₄ (MNPs) were synthesized by availing the co-precipitation technique [34]. Afterwards, the silica coated MNPs (SMNPs) were prepared simply by sol-gel approach by suspending the Fe_3O_4 NPs with tetra-ethyl orthosilicate (TEOS) under vigorous stirring [29]. These SMNPs were modified with (3aminopropyl)triethoxysilane (APTES) to form amine functionalized SMNPs (ASMNPs) with subsequent immobilization of 4-(2-pyridyl) benzaldehyde (PyBz) ligand via Schiff base condensation [35]. Afterwards, homogeneous dimer complex of [Ir(PvBz)₂Cl]₂ was separately synthesized by modification of previously reported protocol [36] and was utilized along with PvBz immobilized nanoparticles (PyBz@ASMNPs) for the synthesis of the final photoredox nanocatalyst of iridium (Ir@PyBz@ASMNPs) [36]. The obtained Ir@PyBz@ASMNPs photoredox nanocatalyst was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectrometry (EDS) and various other physico-chemical techniques. The photocatalytic performance of Ir@PyBz@ASMNPs photoredox nanocatalyst was also studied in detail for C-H arylation of arenes with aryl iodide and oxidative cyanation of tertiary amines. The aforementioned method has potential to fabricate various high performance heterogeneous photoredox nanocatalysts. These photoredox nanocatalysts can be further utilized as a reliable and powerful tool to carry out light promoted organic synthesis under mild conditions in environmentally benign way.

2. Experimental

2.1. Chemicals and reagents

Unless otherwise indicated, all the chemicals were obtained from commercial source and were used without further purifications. Ferric sulphate hydrate and ferrous sulphate heptahydrate were obtained from Central Drug house and Thomas Bakers, respectively. Tetraethyl orthosilicate, (3-aminopropyl) triethoxysilane and iridium chloride were acquired from Alfa Aesar. 4-(2-Pyridyl)benzaldehyde and 1,2,3,4tetrahydroisoqinoline were commercially obtained from TCI. The commercially unavailable substrates, including tetrahydroisoquinolines derivatives were prepared in the lab by utilizing previously reported methods. All the photochemical reactions were under air atmosphere, unless otherwise indicated. The solvents/substrate, like benzene and *p*-xylene were of analytical grade and purified by distillation prior to use. HPLC grade DMSO was dried using activated molecular sieves. Double distilled water was used for the synthetic procedure of material.

2.2. Synthesis of photoredox nanocatalyst

2.2.1. Preparation of magnetically retrievable nanoparticles of Fe_3O_4

Magnetically retrievable nanoparticles of Fe_3O_4 were synthesized by adopting co-precipitation methodology. Initially, $FeSO_4$.7- H_2O (4.2 g) and $Fe_2(SO_4)_3$ (6.0 g) were dissolved in a 500 mL round bottom flask using double distilled water (250 mL) and stirred to obtain a clear orange solution. Afterwards, 15 mL of ammonium hydroxide (25%) was added dropwise to the respected solution to maintain pH 10. The reaction mixture was continuously stirred for a period of 1 h at 60°C to obtain black precipitate of Fe_3O_4 which were separated *via* an external magnet, washed with water and ethanol and further, dried under a vacuum oven at 50 °C [29]. Amount obtained: 2.8 g

2.2.2. Preparation of silica coated magnetically retrievable nanoparticles, SMNPs.

Silica coated MNPs were fabricated by utilizing sol-gel approach using TEOS. In a normal procedure, 0.5 g of Fe_3O_4 nanoparticles were activated by employing 0.1 M HCl solution (2.2 mL). Subsequently, 4:1 v/v ethanol-water (250 mL) mixture was added to the activated Fe_3O_4 and put through sonication for a period of 30 min for the consistent dispersion of the nanoparticles in the solution. Thereafter, 25% NH₄OH solution (5 mL) and TEOS (1 mL) were introduced in the dispersed solution and stirred at 60 °C for 6 h. Lastly, the SMNPs were collected by applying external magnetic force, washed with water and ethanol and dried at 50 °C [29]. Amount obtained: 0.75 g.



Scheme 1. Scheme for the synthesis of Ir@PyBz@ASMNPs based magnetic photoredox nanocatalyst.

2.2.3. Preparation of amine functionalized silica coated magnetically retrievable nanoparticles, ASMNPs.

Amine functionalized silica coated magnetically retrievable nanoparticles, ASMNPs were fabricated by taking 0.2 g of SMNPs in 200 mL of ethanol and sonicated for 30 min. Afterwards, 1 mL of APTES was added dropwise to the resultant solution and subjected to stirring at 60 °C for 6 h to form amine functionalized SMNPs. Subsequently, the synthesized ASMNPs were separated *via* an external magnet, washed with ethanol and kept for drying under a vacuum oven at 50 °C [29]. Amount obtained: 0.19 g.

2.2.4. Preparation of [Ir(PyBz)₂Cl]₂.

A 50 mL round bottom flask equipped with magnetic stir bar was charged with $IrCl_3$ (0.2470 g, 0.8273 mmol), 4-(2-pyridyl) benzaldehyde (0.579 g) and a solution of 2-ethoxy ethanol (19 mL) and water (6.4 mL) was added to dissolve the reactants. The reaction mixture was kept at 125 °C for 16 h under nitrogen atmosphere. After the completion of the reaction, the reaction mixture was cooled to room temperature, filtered and washed with H₂O, ethanol and hexane. The obtained desired bright orange colored compound was dried under vacuum oven and afterwards utilized for next step without further purification [36]. Yield: 75%.

2.2.5. Preparation of PyBz@ASMNPs

4-(2-Pyridyl)benzaldehyde grafted ASMNPs (PyBz@ASMNPs) were synthesized *via* Schiff base condensation. A 250 mL round bottom flask was charged with 100 mg of ASMNPs and 200 mg of 4-(2-pyridyl)benzaldehyde in 150 mL of anhydrous ethanol. The resulting mixture was sonicated for 30 min and afterwards subjected to vigorous stirring at 80 °C for 3 h under nitrogen atmosphere. After completion of the reaction, PyBz@ASMNPs were collected *via* an external magnet, washed with crude ethanol and dried under a vacuum oven for 12 h. Amount obtained: 0.11 g.

2.2.6. Preparation of Ir@PyBz@ASMNPs

The final iridium based photoredox catalyst was synthesized by utilizing PyBz@ASMNPs and [Ir(PyBz)₂Cl]₂. In a 100 mL round bottom flask, PyBz@ASMNPs (110 mg) and [Ir(PyBz)₂Cl]₂ (50 mg) were dissolved in 30 mL of ethylene glycol and subjected to sonication for 30 min. Afterwards, the sonicated solution was heated to 150 °C for 16 h under nitrogen atmosphere. After the completion of the reaction, the desired synthesized catalyst was collected by applying external magnet, washed with ethanol and dried in a vacuum oven for 12 h [36,37]. Amount obtained: 0.11 g.

2.3. Procedure for photocatalytic organic transformations

2.3.1. C-H arylation of arenes with aryl iodide by utilizing photoredox nanocatalyst

A 15 mL glass vial equipped with magnetic stir bar was charged with 1 mmol of aryl iodide substrate, arene (3 mL, 67 equiv), *tert*-potassium butoxide (2 equiv), 35 mg of Ir@PyBz@ASMNPs (0.42 mol%) catalyst in 1 mL DMSO, purged with nitrogen and sealed with rubber cap. Afterwards, the system was sonicated for 15 min and irradiated with the 2×12 W white LEDs by keeping at a distance of 10 cm for 18 h under constant stirring. After completion of the reaction, the catalyst was separated *via* external magnet and the supernatant was extracted with (3 × 30 mL) ethyl acetate and water. Subsequently, the organic layer was collected, rotary evaporated and further purified by silica gel column chromatography using hexane.

2.3.2. Oxidative cyanation of tertiary amines by utilizing photoredox nanocatalyst.

A 15 mL glass vial equipped with magnetic stir bar was charged with 1 mmol of tertiary amine substrate, 1.2 equiv of KCN, 35 mg of Ir@PyBz@ASMNPs (0.42 mol%) catalyst in 1 mL of acetonitrile (MeCN) and sealed with rubber cap. Afterwards, 30% acetic acid (0.3 mL) was added to the mixture *via* syringe to avoid the accidental exposure to the cyanide. Afterwards, the vial was properly sealed with parafilm tape and irradiated with 2×12 W white LEDs by keeping at a distance of 10 cm. The completion of the reaction was monitored by TLC (hexane/ethyl acetate). After completion of the reaction, the catalyst was separated *via* external magnet and the synthesized product was purified by column chromatography using ethyl acetate and hexane (1:9).

Note: The researchers are requested to wear lab coat, safety glasses, mask and nitrile gloves and perform all the reactions in a well-ventilated fume hood to avoid inhalation exposure. Exposure of cyanide poisoning from ingestion and inhalation can be treated by using cyanide antidote kit (amyl nitrite, sodium nitrite and sodium thiosulfate).

Disposal of KCN: Treat the waste with alkaline sodium hypochlorite (household bleach, <1g/L) in excess.

2.4. Analysis

The infrared spectra were analyzed by employing PerkinElmer Spectrum 2000 using KBr pellet method in the range of 4000 to 400 cm⁻¹. UV–Vis spectra have been recorded on a Thermo Scientific absorption spectrophotometer within the wavelength range of 250–800 nm. The photoluminescence (PL) spectroscopy measurements were performed on a FLS980 fluorescence spectrometer (Edinburgh Instruments) with double monochromators on both excitation and emission sides, equipped with a R928P photomultiplier in a thermoelectrically cooled housing (Hamamatsu Photonics), with a 450 W xenon arc lamp as the excitation source for steady-state spectra. Spectral correction curves were provided by Edinburgh Instruments.

Powder sample was mounted on a front face sample holder using a dedicated quartz cell holder.

For time-resolved measurements an EPL-375 ps pulsed diode laser (λ_{em} = 372 nm with a pulse width of 66.5 ps, a repetition rate of 20 MHz, and an average power of 75 μ W; Edinburgh Instruments) in conjunction with a time-correlated single photon counting (TCSPC) system were used.

The obtained PL decay curves were fitted using a threeexponential function:

$$H(t) = \sum_{i=1}^{3} B_i \exp\left(-\frac{t}{\tau_i}\right), \sum_{i=1}^{3} B_i = 1,$$

In this expression, τ_i represent the decay time constants, and B_i represents the normalized amplitudes of each components. The amplitude weighted average decay lifetime τ_{avg} of the entire fluorescence decay process was calculated in the form:

$$\tau_{avg} = \frac{\tau_i B_i}{\sum \tau_i B}$$

PXRD patterns were investigated on a Rigaku Cu (K_{α}) diffractogram at a scan rate of 4 degree per min and 2 θ range of 10– 80to determine the phase, purity and crystalline nature. FEI TECH-NAI G2 T20 transmission electron microscope operated at 200 KV was retained to capture the TEM images of the nanoparticles. The TEM samples were prepared by drop casting a sonicated ethanol suspension of the desired nanoparticles over a carbon coated copper grid. SEM images were recorded on a Tescan MIRA3 FE-SEM microscope. SEM grids were prepared using gold sputtered nanoparticles over a carbon tape placed on a SEM stub. Elemental analysis of the catalyst was investigated using an Ametek EDAX system. Brunauer-Emmett-Teller (BET) method was acquired using an ASI-CT-11 Quantachrome instrument at a degassing temperature of 150 °C to determine the specific surface area, pore volume and pore size distribution. Metal content of the catalyst was measured on Perkin Elmer Avio 200 ICP-OES System. Magnetization of the nanoparticles were confirmed by using a vibrating sample magnetometer (EV-9, Microsense, ADE) in the range of -10000 Oe to 10,000 Oe. The cyclic voltammetry (CV) curve was recorded on an Autolab Potentiostat Galvanostat (AUT204 Netherlands). The measurement was performed utilizing a three-electrode system with ITO coated glass electrode as the working electrode, platinum (Pt) as the counter electrode, and silver-silver chloride (Ag/AgCl) as the reference electrode in PBS solution of pH 7.0 containing 5 mM of $[Fe(CN)_6]^{3-/4-}$. The optimization studies and control experiments were carried out using an Agilent gas chromatograph (6850 GC) having a HP-5MS capillary column (stationary phase: 5% phenyl methyl siloxane; column length: 30 m; internal diameter: 0.25 mm: film thickness: 0.25 um) and a quadrupole mass filter equipped 5975C mass selective detector (MSD) using helium as a carrier gas. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a JEOL JNM-EXCP 400 unless otherwise noted and data are reported in terms of chemical shift related to CDCl₃ (7.26 ppm) or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard, abbreviation used to indicate the multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet), coupling constant (Hz), integration. Thinlayer chromatography (TLC) was performed by utilizing Merck silica gel plates 60 F254 to check the course of reactions and visualized under UV light. Light Source. 12 W Philips white LEDs, Quantity of Light Source: Two

3. Results and discussion

3.1. Characterization of the photoredox nanocatalyst

Characterization of the structure of iridium photoredox nanocatalyst. Ir@PvBz@ASMNPs was verified by employing various physico-chemical techniques. Fourier transform infrared (FT-IR) was carried out to identify the functional groups present at each stage during the synthesis of the catalyst (Fig. S2, see SI for details). The observed photocatalytic result can be correlated with the optical properties of Ir@PyBz@ASMNP photocatalyst; such as UV-Vis diffuse reflectance spectrum, photoluminescence, time resolved photoluminescence (TRPL) analysis and Excitation-emission color map are plotted in **Fig. S3** and **Fig. 2 a**, **b**, **c** respectively. Primarily; UV-Vis spectrum of homogeneous iridium photocatalyst displays an intense absorption peak at 280 nm in the range of 250 nm to 350 nm in MeOH, shows intense absorption from ligand $\pi - \pi^*$ and MLCT transitions **Fig. S3**. The π - π * absorption (singlet-singlet ligand-centered) band for both (homo and hetero) Ir organometallic complex falls in the range 250-320 nm which is an intense ultraviolet band, and closely resembles the spectrum of the free ppy ligand associated with Ir metal center [38,39]. Clear evidence for significant mixing of the singlet and triplet excited states is seen in both the absorption and emission spectra of Ir@PyBz@ASMNPs photo-catalysts. On another note, the weaker absorption band 375 nm that extend to the visible region of low energy is conventionally assigned to metal-to-ligand charge-transfer transitions (³MLCT) (Fig. S3). Both ¹MLCT and ³MLCT bands are typically well observed in both homogeneous and heterogeneous Irorganometallic based complex system. Such absorption spectrum of Ir@PyBz@ASMNPs were well matched and nearly the same as that for $Ir(ppy)_3$ complexes as reported previously [37,40-42].

Furthermore; the separation of photogenerated electrons and holes in Ir@PyBz@ASMNPs generated system was investigated through photoluminescence and time resolved photoluminescence (TRPL) spectroscopy; which showed the steady-state emission spectra excited at 355 nm, the Ir@PyBz@ASMNPs showed strong emission peaks at 430 nm (Fig. 2a). Such observed emission of Ir@PyBz@ASMNPs is due to effective electron transfer process and inhibited recombination of electrons and holes. Such observed phenomenon; eventually promotes electron transfer and reduces the photogenerated electron-hole recombination rate via inhibition of charge carrier recombination [39,42,43]. In addition; Time resolved photoluminescence (TRPL) spectroscopy carried out for Ir@PyBz@ASMNPs photocatalyst; confirms ligand-metal charge transfer lifetimes which showed an average fluorescence decay lifetimes (τ_{ave}) of 13.6 ns. Observed fluorescence decay lifetimes (τ_{ave}) could be well attributed to the emergence of a nonradiative pathway from Ir(ppy)₃ organometallic complexes well supported over heterogeneous system (Fig. 2b) [44] suggesting that photo generated charge carriers survived longer on its surface. The generated sites might be working as a bridge to facilitate the faster electron transfer and enhancing the charge density on Ir centre thus reducing the photocarrier transfer barrier and enabling the photocatalytic activity. On another note; since $Ir(ppy)_3$ based organometallic complexes, are good organic phosphorescent materials system and well known for absorbance due to the large amount of spin-orbit coupling induced by the heavy metal ion [44-46]. The PL excitation – emission map of the Ir@PyBz@ASMNPs is presented in Fig. 2c where Ir based photocatalyst exhibited an excitation-dependent emission since the position of the emission peak widely shifts over a wide range of excitation wavelengths [44-46]. The crystallographic properties and structures of the MNPs and Ir@PyBz@ASMNPs photoredox nanocatalyst were also characterized by X-ray diffraction (XRD). The XRD pattern of the fabricated Ir@PyBz@ASMPs photoredox nanocatalyst exhibited consistency with the peaks of Fe₃O₄ (Fig. S4a) along with the emergence of a new strong diffraction peak at 12.9 corresponding to the IrPC moiety (Fig. S4b) [44,47]. X-ray photoelectron spectroscopy (XPS) was carried out to investigate the surface chemical nature of Ir in Ir@PyBz@ASMNPs. As shown in Fig. 3a, the Ir binding energy spectra displayed two emission peaks at 60.2 eV (Ir $4f_{7/2}$ level) and 63.3 eV (Ir $4f_{5/2}$ level) respectively, which is in agreement with the XPS spectra of Ir 4f region reported in literature and can be attributed to Ir (+3) [15-17,48]. Survey scan and detailed XPS spectra of the elements manifest the presence of Fe 2p, Si 2p, C 1 s, N 1 s and O 1 s in the final Ir@PyBz@ASMNPs (Fig. S5). The transmission electron microscopy (TEM) analysis was carried out to record images of MNPs, SMNPs and Ir@PyBz@ASMNPs (Fig. 3b-d). From the TEM image of MNPs (Fig. 3b), it is evident that MNPs have an average diameter of 13 nm. The inset of Fig. 3b spectacles the selected area electron diffraction pattern (SAED) of MNPs. The bright diffraction rings and white spots points towards the highly crystalline nature of the synthesized magnetic nanoparticles. TEM image of SMNPs reveals a silica coating of about 6 nm in thickness over the MNPs (Fig. 3c). Furthermore, TEM images of MNPs and SMNPs nanoparticles show the spherical morphology of the nanoparticles. In addition, the TEM image in Fig. 3d indicates that Ir@PyBz@ASMNPs have some irregular spherical nanoparticles in the range of 23-26 nm.

Likewise, the SEM images of Ir@PyBz@ASMNPs also reveal that the iridium based photoredox nanocatalyst retains the spherical shape (**Fig. S6**). The qualitative analysis of elements (Fe, Si, C, N, O and Ir) was performed by energy-dispersive X-ray Spectroscopy (EDS) and energy dispersive X-ray Fluorescence (ED-XRF) (**Fig. S7**) while quantitative determination of iridium metal content in the Ir@PyBz@ASMNPs was accomplished by ICP-OES and was found to be 0.1207 mmol g⁻¹. The magnetization properties of the MNPs, SMNPs and Ir@PyBz@ASMNPs were recorded by using vibratingsample magnetometer (VSM) at room temperature (300 K) (**Fig. S8**). The saturation magnetization, Ms value of the Ir@PyB-



Fig. 2. a) PL excitation ($\lambda_e x = 355$ nm, black line) and PL emission ($\lambda_e m = 430$ nm, red line) spectra, b) PL decay collected at the emission maximum. Experimental data are represented by symbols, whereas a solid line is a three-exponential fit (see the Experimental section for details) and c) Excitation-emission color map. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. a) XPS spectra of Ir@PyBz@ASMNPs photoredox nanocatalyst, TEM images of b) MNPs; inset: SAED pattern of MNPs, c) SMNPs and d) Ir@PyBz@ASMNPs photoredox nanocatalyst.

z@ASMNPs photoredox nanocatalyst is found to be 27.6 emu/g which is sufficient enough for the magnetic separation of the photoredox nanocatalyst from the dispersed reaction mixture with a simple external magnet within the time period of 40 sec.

To investigate the redox potential of the Ir@PyBz@ASMNPs, cyclic voltammetry experiment (CV) was performed in the presence of 5 mM [Fe(CN)₆]^{3-/4-} containing PBS (Phosphate buffer saline) at pH 7 at a scan rate of 0.1 V/s in potential range from -1.0 V to

1.0 V. As seen from curve in Fig. 4, the Ir@PyBz@ASMNPs exhibited well defined characteristic redox peaks at -0.16266 and 0.40863 V [49,50]. TGA curve illustrates that the weight loss of Ir@PyB-z@ASMNPs (13 %) mainly occurs in the temperature range of 23-150 °C due to the volatilization of adsorbed water. It is evident from the results that our fabricated photoredox Ir@PyBz@ASMNPs nanocatalyst is thermally stable and only 29 % weight loss occurs up to the temperature of 600 °C (Fig. S9). The Brunauer–Emmet



Fig. 4. Cyclic voltammetry curve of Ir@PyBz@ASMNPs at a scan rate of 0.1 V/s.

t–Teller (BET) analysis reveal that Ir@PyBz@ASMNPs photoredox catalyst has specific surface area of 5.298 \times 10 m^2g^{-1} and average pore diameter of 7.201E + 01 Å.

3.2. Catalytic activity

To date, many groups have reported the C-C bond formation using various photoredox catalysts (**Table S1a**). However, these

Table 1

Optimization of C-H arylation of arene with aryl iodide.^{a.}

methodologies exhibit various challenges such as high cost, time consuming separation, transition metal impurity in the final product, formation of undesired, toxic and stoichiometric side products, involvement of high power consuming white light sources (Xenon lamp with power more than 100 W) as well as destructive nature of UV radiation and harsh reaction conditions. Herein, we employed the heterogeneous Ir@PyBz@ASMNPs photoredox nanocatalyst for the C-H arylation, appealing to the principles of sustainable chemistry. Initially, we commenced our studies by probing the C-H arylation of unactivated benzene using iodobenzene as the model reaction for optimizing the reaction conditions. Notably, a control experiment was initially performed with various solvent systems. Unfortunately, unsatisfactory results were obtained with acetonitrile (ACN) and methanol (MeOH) (Table 1, entries 1 and 2). Nevertheless, superior results were observed when the reaction was performed in dimethyl sulfoxide (DMSO) (Table 1, entry 3). Additionally, presence of water in DMSO drastically hampered the catalytic progress of the reaction and no desired product was obtained. (Table 1, entry 4). Further, effect of various inorganic and organic bases, such as K₂CO₃ (Table 1, entry 5), Cs₂CO₃ (entry 6) and triethylamine (Table 1, entry 7) was also examined and the best performance was attained with *t*-KOBu (Table 1, entry 3). The unique catalytic performance is particularly noticeable when Ir@PyBz@ASMNPs is excluded, as only 38% yield of the desired biphenyl was afforded (Table 1, entry 8). Almost no product was formed on carrying out the reaction under the dark conditions (Table 1, entry 9).

Therefore, control reactions disclosed that the heterogeneous photoredox nanocatalyst (Ir@PyBz@ASMNPs), white light

	+ in <u>Ir@PyBz@ASMNPs, Base</u> , /				
Entry	Catalyst (mg)	Base (2 equiv)	Solvent (1 mL)	Time (h)	Yield ^b (%)
	Ir@PyBz@ASMNPs (0.42 mol%, 35 mg)	<i>t</i> -KOBu	ACN	24	-
2.	Ir@PyBz@ASMNPs (0.42 mol%, 35 mg)	t-KOBu	MeOH	24	34
3.	Ir@PyBz@ASMNPs (0.42 mol%, 35 mg)	t-KOBu	DMSO	24	>99
4.	Ir@PyBz@ASMNPs (0.42 mol%, 35 mg)	t-KOBu	DMSO:H ₂ O (1:1)	24	0
5.	Ir@PyBz@ASMNPs (0.42 mol%, 35 mg)	K ₂ CO ₃	DMSO	24	0
6.	Ir@PyBz@ASMNPs (0.42 mol%, 35 mg)	Cs ₂ CO ₃	DMSO	24	-
7.	Ir@PyBz@ASMNPs (0.42 mol%, 35 mg)	Triethylamine	DMSO	24	0
8.	-	t-KOBu	DMSO	24	38
9.	Ir@PyBz@ASMNPs (0.42 mol%, 35 mg)	t-KOBu	DMSO	24	Trace ^c
10.	Ir@PyBz@ASMNPs (0.42 mol%, 35 mg)	t-KOBu	DMSO	24	72 ^u
11.	Ir@PyBz@ASMNPs (0.3 mol%, 25 mg)	t-KOBu	DMSO	24	91
12.	Ir@PyBz@ASMNPs (0.6 mol%, 70 mg)	t-KOBu	DMSO	24	95
13.	Ir@PyBz@ASMNPs (0.3 mol%, 35 mg)	t-KOBu	DMSO	24	04
14.	lr@PyBz@ASMNPs (0.42 mol%, 35 mg)	t-KOBu	DMSO	18	97
15.	Ir@PyBz@ASMNPs (0.42 mol%, 35 mg)	<i>t</i> -KOBu	DMSO	12	83
16	Homogeneous IrPC (0.5 mol%)	<i>t</i> -KOBu	DMSO	18	>99

^a Reaction conditions: iodo-benzene (1 mmol), benzene (67 equiv, 3 mL), solvent (1 mL), 25 °C, two 12 W white LEDs, N₂ atm. ^bGC-MS yield. ^cDark. ^d12 W white LEDs. ^eAir.

 $(2 \times 12 \text{ W})$, and *t*-KOBu were all necessary individually to execute the reaction. However, over irradiation using 12 W white LED light instead of 2×12 W for 24 h led to the reduction in the yield (72%) of the desired biphenyl (Table 1, entry 10). Afterwards, decreasing the amount of catalyst from 35 mg to 25 mg led to decline in the product yield (Table 1, entry 11). Further, on increasing the amount of catalyst from 35 mg to 70 mg, slight decrease in the yield was observed which could be accredited to the interference of the mass transfer between the active sites and reagent caused by the low dispersity of the excess catalyst in the reaction media or low dispersity of light due to fouling of vial (Table 1, entry 12). Moreover, reaction in the absence of inert atmosphere did not proceed at all (Table 1, entry 13). Furthermore, running the reaction for 18 h instead of 24 h provides comparable yield (Table 1, entry 14). Although, significant decrease in yield was observed on further decreasing the reaction time to 12 h (Table 1, entry 15). Additionally, we have also utilized homogeneous iridium photoredox catalyst (IrPC) which disclosed that upon immobilization of the photocatalyst over heterogeneous support, no significant change in the efficiency of the catalyst was observed (Table 1, entry 16). In view of the above findings, a series of aryl halides were also scrutinized under continuous visible light excitation which indicates the decrease in yield of the desired product in the order of iodide, bromide and chlorides that could be probably due to the different bond dissociation energies (Table S2, see SI for details).

3.3. Substrate scope

Following the establishment of the optimized standard conditions (Table 1, entry 14), substrate scope of the photocatalytic C-H arylation of various aryl iodide substrates was explored to demonstrate the applicability of the reaction with the fabricated Ir@PyBz@ASMNPs photoredox nanocatalyst. Initially, we focused on various para substituted electron donating aryl iodides which exhibited good to excellent yields (Scheme 2, 3a-c). Moreover, the meta substituted electron donating aryl iodides were well tolerated for the reaction and furnished the desired product in good yield (Scheme 2, 3d, 3e). The ortho substituted electron donating aryl iodides delivered the desired product in low yield and revealed the impact of steric hinderance over the reaction (Scheme 2, 3**f-h**). The results conclude that the vield of the coupling products increases progressively in the order of o- to m- to *p*- substituted arvl iodides. Likewise, the electron withdrawing groups positioned at para position such as -NO₂, -F and -CF₃ are also withstand well and provided good yields (Scheme 2, 3i-k).

Further analysis was carried out to deduce a plausible mechanism for the SET initiated C-H arylation reaction. The mechanistic experiment suggests that in the presence of radical scavenger (TEMPO (1.5 equiv)) (Scheme 3), the C-H arylation transformation is completely inhibited, consistent with a mechanism in which ion radicals initiate the reaction.



Scheme 2. Substrate scope for C-H arylation of arenes with aryl iodide using Ir@PyBz@ASMNPs based photoredox nanocatalyst.^a. ^aReaction conditions: aryl halide (1 mmol), aryl (67 equiv, 3 mL), *t*-KOBu (2 equiv), DMSO (1 mL), Ir@PyBz@ASMNPs (0.42 mol%, 35 mg), 25 C, two 12 W white LEDs, 18 h, N₂ atm., isolated yield. ^bGC-MS yield; TOF = TON per hour (TON is the number of moles of the product per mole of the catalyst).



Scheme 3. Mechanistic control experiment.

3.4. Plausible mechanism

Previously reported kinetic isotope effect (KIE) studies in various literatures suggest that the C-H cleavage of benzene is not the rate determining step [51–53]. On the basis of above mentioned experiments and previous literature precedents, a tentative mechanism is proposed for the activation of aryl halide by SET from visible-light excited photoredox catalyst, Ir(III)*@PyBz@ASMNPs (Scheme 4). The generated aryl halide radical anion (Ar-X^{•-}) further undergoes mesolytic fragmentation to form aryl radical by the fragmentation of halogen anion. Afterwards, the radical (Ar-) undergo coupling reaction with another aryl molecule to form the key transition state of biaryl radical anion. Subsequently, the intermediate is further deprotonated by the base to afford the biaryl radical anion. Finally, the highly reductive biaryl radical anion undergoes oxidation via donating an electron to the oxidized Ir(IV)@PyBz@ASMNPs photoredox nanocatalyst to provide the targeted biaryl product and to complete the catalytic cycle [54].

To our delight, the versatile Ir@PyBz@ASMNPs photoredox nanocatalyst was not limited to the C-H arylation of aryl iodides. We further probed the photoredox nanocatalyst to carry out the oxidative Strecker reaction via C-H activation to construct biologically important α -amino nitriles which are the key intermediates of α -amino carbonyl compounds and 1,2-diamines. Notably, the cyano functionalized tertiary amines can further be utilized as starting materials for the synthesis of vitally important heterocyclic and carbocyclic molecules used in pharmacological and biological compounds [55]. The valuable α -amino nitriles were synthesized by employing the previously reported optimized conditions by Rueping and co-workers [56]. Primarily, we carried out the regioselective reaction with a set of cyclic tertiary amines which illustrated excellent functional group compatibility and afforded the resulting products in good to excellent yield (Scheme 5, 5a-c). The results point toward the wider utility and generality of our synthesized iridium catalyst. Conversely, this



Scheme 4. Proposed mechanism of the photoredox homolytic aromatic substitution.

reaction cannot be extended to heteroatomic amines which afforded unpredictable compounds (Scheme 5, 5**d**).

3.5. Catalytic reusability test

The long lifetime, recyclability and reusability of heterogeneous catalyst are some of the significant milestones towards achieving the goal of green and sustainable chemistry. Henceforth, we turn our attention towards the reusability of the photoredox nanocatalyst and investigated the catalytic durability of Ir@PyBz@ASMNPs with the model C-H arylation reaction under optimized reaction conditions. After completion of the reaction, the Ir@PyBz@ASMNPs catalyst was separated, washed with absolute ethanol, dried in vacuo overnight prior to use and it was subjected to the subsequent recycle runs under the same reaction conditions (Fig. 5a). The catalytic reusability test of the fabricated magnetic Ir@PyBz@ASMNPs photoredox nanocatalyst suggests that the catalyst can be reused with high selectivity, although the rate of reaction decreases. The TEM analysis (Fig. 5c), FT-IR (Fig. S11), VSM analysis (Fig. S12), SEM (Fig. S13b) and ED-XRF (Fig. S14) unveiled no noteworthy physical and chemical change in the structure and morphology of the Ir@PyBz@ASMNPs and the photoredox nanocatalyst was preserved even after five consecutive runs.

ICP analysis of the mother liquor after the first cycle revealed only negligible leaching of the Ir species (<0.1%). However, the decrease in catalyst efficiency from third run onwards upon reuse could be attributed to the partial conversion of Ir (III) to Ir (IV) which was further confirmed by XPS analysis of the reused catalyst. The XPS analysis of recovered catalyst after five cycles (**Fig. S15f**) suggested that during the catalytic cycle, Ir (III) got partially converted to Ir (IV). The doublet component at 61.30 (4f_{7/2}) and 64.28 (4f_{5/2}) was attributed to Ir (III), while the doublet at 62.65 and 65.64 eV to Ir (IV) oxidized state [57].

Our group further envisions to work towards regenerating the catalyst [58–60] completely to fully explore its potential by employing various reducing species such as triethylamine [61] as an electron donor, non-heme iron (IV) oxo complex *via* a photon coupled electron transfer [62] etc. responsible for the restoration of photoactive state.

3.6. Leaching test

In order to examine the heterogeneous nature of the fabricated Ir@PyBz@ASMNPs catalyst, leaching test was carried out for the C-H arylation of arenes with aryl iodide under the optimized reaction conditions. After 9 h, catalyst was magnetically separated from the reaction mixture and the reaction mixture was evaluated using GCMS which revealed that only 52% conversion was achieved. Further exposing the reaction mixture with light in absence of catalyst and continuous stirring showed only 63% conversion of the desired product which indicates that there is negligible leaching of the active species in the supernatant. Moreover, the leaching of the iridium species from the heterogeneous catalyst was also analyzed *via* ICP-OES analysis which revealed that<0.07 % of iridium of the initially added catalyst was leached from the surface during the course of the reaction.



Scheme 5. Substrate scope for Ir@PyBz@ASMNPs based photoredox nanocatalyst mediated α -cyanation of tertiary amines.^a aReaction conditions: tertiary amine (1 mmol), KCN (1.2 equiv), 30% acetic acid (AcOH) (0.3 mL), Ir@PyBz@ASMNPs (0.42 mol%, 35 mg), MeCN (1 mL), 25 °C, two 12 W white LEDs, air, isolated yield, 12 h. ^bTMSCN as cyanation source. ^cTOF = TON per hour (TON is the number of moles of the product per mole of the catalyst).



Fig. 5. a) Reusability test of Ir@PyBz@ASMNPs for the C-H arylation of arenes with aryl iodide; TEM images of b) fresh and c) reused Ir@PyBz@ASMNPs catalyst.

4. Conclusions

In this study, we have fabricated a magnetically retrievable iridium complex surface engineered over the silica coated Fe_3O_4 and demonstrated its effectiveness as an effective visible light photocatalyst for C-H arylation as well as C-H cyanation. The Ir@PyBz@ASMNPs shows high surface area, thermal and chemical stability and can be recovered and reused up to five runs without any significant decrease in the catalytic activity for visible light mediated organic reactions at room temperature and atmospheric pressure. The proposed radical mechanism is reinforced by the intensely reduced reaction rate in the presence of TEMPO scavenger (as radical trapping agent). The catalyst embraces great potential as substitute of the homogeneous catalysts and provides a green and sustainable chemical route. We envisioned that the surface engineering protocol over nano sized magnetic core described in this article could be easily implemented to gain access to numerous sustainable and heterogeneous photoredox nanocatalysts derived from metal polypyridyl complexes by rationally tuning the peripheral ligands toward specific catalytic reactions. The study of various photophysical and electrochemical properties of this new CHO– functionalized Iridium based photoredox nanocatalyst are underway in our laboratory. We envision that this work has promising scope of utilizing iridium as a photoredox nanocatalyst and we are highly motivated to study the regeneration strategies for promoting visible-light photocatalysis towards industrial scale applicability under ambient conditions.

CRediT authorship contribution statement

Pooja Rana: Investigation, Data curation, Writing – original draft, Methodology. **Rashmi Gaur:** Conceptualization, Visualization. **Bhawna Kaushik:** Validation, Data curation, Writing – original draft, Visualization. **Pooja Rana:** Formal analysis, Writing – review & editing. **Sneha Yadav:** Validation, Writing – review & editing. **Priya Yadav:** Validation, Writing – review & editing. **Priya Yadav:** Validation, Writing – review & editing. **Priya Sub Priya S**

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The work was supported by the Department of Science and Technology (DST) (Grant ID: DST/TMD-EWO/WTI2K19/EWF H/2019/290(G)) to design a commercial scale photoreactor. Pooja Rana, Bhawna Kaushik, Pooja Rana, Sneha Yadav and Priya Yadav gratefully acknowledge CSIR and UGC, Delhi, India for awarding research fellowships. Moreover, the authors also thank USIC-CLF, DU for FT-IR, XRD, VSM analysis, PerkinElmer (Mumbai) for ICP-OES analysis and TERI (Gurugram, India) for TEM analysis.

Appendix A. Supplementary material

Supporting Information contains UV-Vis analysis, TEM image, SEM image, ED-XRF analysis, XPS, VSM curves and TGA of fresh and recovered catalyst, Reusability test of catalyst, Literature precedence table. NMR data and spectra. GC-MS Spectra. Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2021.08.014.

References

- B. Zhang, L. Sun, Artificial Photosynthesis: Opportunities and Challenges of Molecular Catalysts, Chem. Soc. Rev. 48 (2019) 2216–2264.
- [2] K. Nakata, A. Fujishima, TiO₂ Photocatalysis: Design and Applications, J. Photochem. Photobiol., C 13 (3) (2012) 169–189.
- [3] C.R. Stephenson, T.P. Yoon, D.W. MacMillan, Visible Light Photocatalysis in Organic Chemistry, John Wiley & Sons, 2018.
- [4] R.K. Sharma, P. Yadav, M. Yadav, R. Gupta, P. Rana, A. Srivastava, R. Zbořil, R.S. Varma, M. Antonietti, M.B. Gawande, Recent Development of Covalent Organic Frameworks (COFs): Synthesis and Catalytic (Organic-Electro-Photo) Applications, Mater. Horiz. 7 (2020) 411–454.
- [5] C. Chen, W. Ma, J. Zhao, Semiconductor-Mediated Photodegradation of Pollutants under Visible-Light Irradiation, Chem. Soc. Rev. 39 (11) (2010) 4206, https://doi.org/10.1039/b921692h.
- [6] C.K. Prier, D.A. Rankić, D.W. MacMillan, Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis, Chem. Rev. 113 (2013) 5322–5363.

- [7] B. Sahoo, Visible Light Photocatalyzed Redox-Neutral Organic Reactions and Synthesis of Novel Metal-Organic Frameworks, Springer, 2016.
- [8] M.H. Shaw, J. Twilton, D.W.C. MacMillan, Photoredox Catalysis in Organic Chemistry, J. Org. Chem. 81 (16) (2016) 6898–6926.
- [9] J.M. Narayanam, C.R. Stephenson, Visible Light Photoredox Catalysis: Applications in Organic Synthesis, Chem. Soc. Rev. 40 (2011) 102–113.
- [10] N. Corrigan, S. Shanmugam, J. Xu, C. Boyer, Photocatalysis in Organic and Polymer Synthesis, Chem. Soc. Rev. 45 (22) (2016) 6165–6212.
- [11] D. Rackl, P. Kreitmeier, O. Reiser, Synthesis of a Polyisobutylene-tagged fac-Ir (ppy)₃ complex and its Application as Recyclable Visible-Light photocatalyst in a Continuous Flow Process, Green Chem. 18 (1) (2016) 214–219.
- [12] K. Teegardin, J.I. Day, J. Chan, J. Weaver, Advances in Photocatalysis: A Microreview of Visible Light mediated Ruthenium and Iridium Catalyzed Organic Transformations, Org. Process Res. Dev. 20 (2016) 1156–1163.
- [13] A. Savateev, M. Antonietti, Heterogeneous Organocatalysis for Photoredox Chemistry, ACS Catal. 8 (10) (2018) 9790–9808.
- [14] C. Xu, P. Ravi Anusuyadevi, C. Aymonier, R. Luque, S. Marre, Nanostructured Materials for Photocatalysis, Chem. Soc. Rev. 48 (14) (2019) 3868–3902.
- [15] S. Zhang, M. Li, Q. Wu, H. Yang, J. Han, H. Wang, X. Liu, Photocatalytic Hydrogen Evolution from Formate and Aldehyde over Molecular Iridium Complexes stabilized by Bipyridine-Bridging Organosilica Nanotubes, Appl. Catal., B 236 (2018) 466–474.
- [16] Z.-Y. Xu, Y.i. Luo, D.-W. Zhang, H. Wang, X.-W. Sun, Z.-T. Li, Iridium Complex-Linked Porous Organic Polymers for Recyclable, Broad-scope Photocatalysis of Organic Transformations, Green Chem. 22 (1) (2020) 136–143.
- [17] G.H. Gunasekar, S. Yoon, A Phenanthroline-based Porous Organic Polymer for the Iridium-Catalyzed Hydrogenation of Carbon Dioxide to Formate, J. Mater. Chem. A 7 (23) (2019) 14019–14026.
- [18] B. An, L. Zeng, M. Jia, Z. Li, Z. Lin, Y. Song, Y. Zhou, J. Cheng, C. Wang, W. Lin, Molecular Iridium Complexes in Metal-Organic Frameworks Catalyze CO₂ Hydrogenation via Concerted Proton and Hydride Transfer, J. Am. Chem. Soc. 139 (49) (2017) 17747–17750.
- [19] J. Ma, F. Strieth-Kalthoff, T. Dalton, M. Freitag, J.L. Schwarz, K. Bergander, C. Daniliuc, F. Glorius, Direct Dearomatization of Pyridines via an Energy-Transfer-Catalyzed Intramolecular [4+2] Cycloaddition, Chem 5 (11) (2019) 2854–2864.
- [20] M. Simonetti, D.M. Cannas, I. Larrosa, Biaryl Synthesis via C-H Bond Activation: Strategies and Methods, in Advances in Organometallic Chemistry, Elsevier (2017) 299–399.
- [21] F. Kloss, T. Neuwirth, V.G. Haensch, C. Hertweck, Metal-free synthesis of pharmaceutically important biaryls by photosplicing, Angew. Chem. Int. Ed. 130 (44) (2018) 14684–14689.
- [22] S. Yuan, J. Chang, B. Yu, Construction of biologically important biaryl scaffolds through direct C-H bond activation: advances and prospects, Top. Curr. Chem. 378 (2020) 1–70.
- [23] K.M. Saini, R.K. Saunthwal, A.K. Verma, Pd-Catalyzed One-Pot Sequential Cross-coupling reactions of Tetrabromothiophene, Org. Biomol. Chem. 15 (48) (2017) 10289–10298.
- [24] F.X. Felpin, S. Sengupta, Biaryl synthesis with arenediazonium salts: crosscoupling, CH-arylation and annulation reactions, Chem. Soc. Rev. 48 (2019) 1150–1193.
- [25] A.K. Rathi, M.B. Gawande, J. Pechousek, J. Tucek, C. Aparicio, M. Petr, O. Tomanec, R. Krikavova, Z. Travnicek, R.S. Varma, Maghemite Decorated with Ultra-Small Palladium Nanoparticles (γ-Fe₂O₃-Pd): Applications in the Heck-Mizoroki Olefination, Suzuki Reaction and Allylic Oxidation of alkenes, Green Chem. 18 (2016) 2363–2373.
- [26] I. Hussain, T. Singh, Synthesis of Biaryls through Aromatic C-H Bond Activation: A Review of Recent Developments, Adv. Synth. Catal. 356 (8) (2014) 1661–1696.
- [27] S.E. Hooshmand, B. Heidari, R. Sedghi, R.S. Varma, Recent advances in the suzuki-miyaura cross-coupling reaction using efficient catalysts in ecofriendly media, Green Chem. 21 (3) (2019) 381–405.
- [28] I. Ghosh, L. Marzo, A. Das, R. Shaikh, B. König, visible light mediated photoredox catalytic arylation reactions, Acc. Chem. Res. 49 (8) (2016) 1566–1577.
- [29] P. Rana, R. Gaur, R. Gupta, G. Arora, A. Jayashree, R.K. Sharma, Cross-Dehydrogenative C(sp³)–C(sp³) coupling via C-H Activation using Magnetically Retrievable Ruthenium-based Photoredox Nanocatalyst under Aerobic Conditions, Chem. Commun. 55 (51) (2019) 7402–7405.
- [30] R. Gupta, M. Yadav, R. Gaur, G. Arora, P. Rana, P. Yadav, A. Adholeya, R.K. Sharma, Silica-Coated Magnetic-Nanoparticle-Supported DABCO-Derived Acidic Ionic Liquid for the Efficient Synthesis of Bioactive 3, 3-Di (indolyl) indolin-2-ones, ACS Omega 4 (25) (2019) 21529–21539.
- [31] P. Yadav, M. Yadav, R. Gaur, R. Gupta, G. Arora, P. Rana, A. Srivastava, R.K. Sharma, Fabrication of copper-based silica-coated magnetic nanocatalyst for efficient one-pot synthesis of chalcones via ^A3 coupling of aldehydes-alkynesamines, ChemCatChem 12 (9) (2020) 2488–2496.
- [32] M.B. Gawande, P. Fornasiero, R. Zbořil, Carbon-Based Single-Atom Catalysts for Advanced Applications, ACS Catal. 10 (3) (2020) 2231–2259.
- [33] M.B. Gawande, P.S. Branco, R.S. Varma, Nano-magnetite (Fe₃O₄) as a support for recyclable catalysts in the development of sustainable methodologies, Chem. Soc. Rev. 42 (8) (2013) 3371, https://doi.org/ 10.1039/c3cs35480f.
- [34] R. Gaur, M. Yadav, R. Gupta, G. Arora, P. Rana, R.K. Sharma, Aerobic Oxidation of Thiols to Disulfides by Silver-Based Magnetic Catalyst, ChemistrySelect 3 (9) (2018) 2502–2508.

- [35] R.K. Sharma, A. Puri, Y. Monga, A. Adholeya, Acetoacetanilide-functionalized Fe₃O₄ nanoparticles for selective and cyclic removal of Pb²⁺ ions from different charged wastewaters, J. Mater. Chem. A 2 (32) (2014) 12888–12898.
- [36] W.-J. Yoo, S. Kobayashi, Efficient Visible Light-Mediated Cross-Dehydrogenative Coupling Reactions of Tertiary Amines Catalyzed by a Polymer-Immobilized Iridium-based Photocatalyst, Green Chem. 16 (5) (2014) 2438–2442.
- [37] A. Singh, K. Teegardin, M. Kelly, K.S. Prasad, S. Krishnan, J.D. Weaver, Facile synthesis and complete characterization of homoleptic and heteroleptic cyclometalated iridium (III) complexes for photocatalysis, J. Organomet. Chem. 776 (2015) 51–59.
- [38] W. Zhao, F.N. Castellano, Upconverted emission from pyrene and Di-tertbutylpyrene using Ir (ppy)₃ as triplet Sensitizer, J. Phys. Chem. A 110 (40) (2006) 11440–11445.
- [39] G.J. Hedley, A. Ruseckas, I.D.W. Samuel, Ultrafast luminescence in Ir(ppy)₃, Chem. Phys. Lett. 450 (4-6) (2008) 292–296.
- [40] M.S. Mehata, Y. Yang, Z.J. Qu, J.S. Chen, F.J. Zhao, K.L. Han, Spin Mixed Charge Transfer states of Iridium Complex Ir(ppy)₃: Transient Absorption and Time-Resolved Photoluminescence, RSC Adv. 5 (2015) 34094–34099.
- [41] X. Meng, R. Bai, X. Wang, F. Pan, L. He, Red to Blue Emitting Cationic Iridium Complexes with 2-phenyl-4-dimethylaminopyridine as the Cyclometalating Ligand: Synthesis Characterization and Electroluminescent devices, Dyes Pigm. 165 (2019) 458–466.
- [42] T. Tsuboi, M. Tanigawa, Optical characteristics of PtOEP and Ir(ppy)₃ tripletexciton materials for organic electroluminescence devices, Thin Solid Films 438 (2003) 301–307.
- [43] E.C. Constable, C.D. Ertl, C.E. Housecroft, J.A. Zampese, Green-emitting iridium (iii) complexes containing sulfanyl or sulfone-functionalized cyclometallating 2-phenylpyridine ligands, Dalton Trans. 43 (2014) 5343–5356.
- [44] H. Wang, Q. Liao, H. Fu, Y. Zeng, Z. Jiang, J. Ma, J. Yao, Ir(ppy)₃ phosphorescent microrods and nanowires: promising micro-phosphors, J. Mater. Chem. 19 (2009) 89–96.
- [45] R. Holmes, S. Forrest, Y.J. Tung, R.C. Kwong, J.J. Brown, S. Garon, M.E. Thompson, Appl. Phys. Lett. 82 (2003) 2422.
- [46] M. Baldo, M.E. Thompson, S. Forrest, High-efficiency fluorescent organic lightemitting devices using a phosphorescent sensitizer, Nature 403 (2000) 750– 753.
- [47] C. Murawski, C. Elschner, S. Lenk, S. Reineke, M.C. Gather, Investigating the molecular orientation of Ir(ppy)₃ and Ir(ppy)₂(acac) emitter complexes by Xray diffraction, Org. Electron. 53 (2018) 198–204.
- [48] Z. Hao, S. Li, J. Sun, S. Li, F. Zhang, Efficient Visible-Light-Driven Depolymerization of Oxidized Lignin to Aromatics Catalyzed by an Iridium Complex Immobilized on Mesocellular Silica Foams, Appl. Catal., B 237 (2018) 366–372.

- [49] X. Kang, J. Liu, H. Tian, C. Zhang, B. Yang, Y. NuLi, H. Zhu, C. Yang, Controlled activation of iridium film for AIROF microelectrodes, Sens. Actuators, B 190 (2014) 601–611.
- [50] X. Miao, C. Yang, C.H. Leung, D.L. Ma, Application of Iridium (III) complex in Label-Free and Non-Enzymatic Electrochemical Detection of Hydrogen Peroxide based on a Novel "on-off-on" Switch Platform, Sci. Rep. 6 (2016) 25774.
- [51] Z. Xu, Li. Gao, L. Wang, M. Gong, W. Wang, R. Yuan, Visible Light Photoredox Catalyzed Biaryl Synthesis using Nitrogen Heterocycles as Promoter, ACS Catal. 5 (1) (2015) 45–50.
- [52] W. Wu, E. Cui, Y. Zhang, C. Zhang, F. Zhu, C.-H. Tung, Y. Wang, Involving Single-Atom Silver (0) in Selective Dehalogenation by AgF under Visible-Light Irradiation, ACS Catal. 9 (7) (2019) 6335–6341.
- [53] X. Zheng, L. Yang, W. Du, A. Ding, H. Guo, Amine-Catalyzed Direct Photoarylation of Unactivated Arenes, Chem. Asian J. 9 (2) (2014) 439–442.
- [54] Y. Cheng, X. Gu, P. Li, Visible-light Photoredox in Homolytic Aromatic Substitution: Direct Arylation of Arenes with Aryl Halides, Org. Lett. 15 (2013) 2664–2667.
- [55] V. V. Kouznetsov, C. E. P. Galvis, Strecker Reaction and α-amino nitriles: Recent Advances in their Chemistry, Synthesis, and Biological Properties, Tetrahedron, 74 (2018) 773–810.
- [56] M. Rueping, S. Zhu, R.M. Koenigs, Visible-Light Photoredox Catalyzed Oxidative Strecker Reaction, Chem. Commun. 47 (47) (2011) 12709, https://doi.org/ 10.1039/c1cc15643h.
- [57] Z. Zhu, X. Liu, Z. Ye, J. Zhang, F. Cao, J. Zhang, A Fabrication of Iridium Oxide film pH Micro-Sensor on Pt Ultramicroelectrode and its Application on in-situ pH Distribution of 316L Stainless Steel Corrosion at Open Circuit Potential, Sens. Actuators, B 255 (2018) 1974–1982.
- [58] T. Pintauer, Catalyst Regeneration in Transition-Metal-Mediated Atom-Transfer Radical Addition (ATRA) and Cyclization (ATRC) Reactions, Eur. J. Inorg. Chem. 2010 (17) (2010) 2449–2460.
- [59] K.E. Allen, D.M. Heinekey, A.S. Goldman, K.I. Goldberg, Regeneration of an Iridium (III) Complex Active for Alkane Dehydrogenation using Molecular Oxygen, Organomet. 33 (6) (2014) 1337–1340.
- [60] L. Capaldo, D. Ravelli, The dark side of photocatalysis: one thousand ways to close the cycle, Eur. J. Org. Chem. 19 (2020) 2783–2806.
- [61] J.M. Kern, J.P. Sauvage, Photoassisted C-C coupling via Electron Transfer to Benzylic Halides by a Bis(di-imine) Copper (I) Complex, Chem. Commun. 8 (1987) 546–548.
- [62] Y. Nishida, Y. Morimoto, Y.-M. Lee, W. Nam, S. Fukuzumi, Effects of proton acceptors on formation of a Non-Heme Iron (IV)–oxo Complex via Proton-Coupled electron transfer, Inorg. Chem. 52 (6) (2013) 3094–3101.