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Encapsulating Au-Fe_3O_4 Nanodots into AIE active Supramolecular Assemblies: Ambient Visible light Harvesting “Dip-Strip” Photocatalyst for C-C /C–N Bond Formation Reactions

Harpreet Kaur, ‡ Mandeep Kaur, ‡ Preet Kamal Walia, ‡ Manoj Kumar and Vandana Bhalla*

Abstract: The present study demonstrates the development of supramolecular porous ensemble consisting of hetero-oligophenylene derivative **6** and **Au-Fe_3O_4** nanodots. Supramolecular assemblies of AIE active hetero-oligophenylene derivative **6** served as reactors for the generation of **Au-Fe_3O_4** nanodots. The as prepared supramolecular ensemble functioned as an efficient recyclable photocatalytic system for C(sp^2)−H bond activation of anilines for the construction of quinoline carboxylates. Interestingly, the ‘dip catalyst’ prepared by depositing **PTh-*co*-PANI-6: Au-Fe_3O_4** nanodots on a filter paper which served as a recyclable strip (upto 10 cycles) for C-C/C-N bond formation reaction.

Introduction

Among various magneto-plasmonics, gold-iron oxide (Au-Fe_3O_4) nanocomposites are particularly attractive due to their remarkable photocatalytic activities in C-C/ C-N bond formation reactions.[1] The combination of magnetic Fe_3O_4 and Au nanoparticles not only tuned the efficiency of the system but also improve the recyclability/reusability of the catalytic system. The photocatalytic efficiency of the system is also influenced by the photophysical properties of the supporting organic materials. The supporting organic materials also control various other functions such as stability, dissolution and biocompatibility of the metal NPs.[2] These hybrid materials comprising supporting materials and Au-Fe_3O_4 nanocomposites provide an efficient and atom economical approach for the construction of C-C/ C-N bond formation. Over the past few years, a lot of research efforts are centred around the development of new strategies for improving the photocatalytic efficiency of Au-Fe_3O_4 nanocomposites.[3] Though the supporting organic materials play an important role in increasing the activity of the system yet most of the research efforts are mainly focused at improvement of catalytic efficiency by controlling the size and shape of the nanomaterials and relatively less efforts are done to examine the role of structural modification/photophysical properties of the supporting organic materials. To investigate the role of supporting materials in enhancing the catalytic activity of the system, a study relating to structural modifications of stabilizing species and catalytic efficiency of the system is needed. Moreover, most of the reported synthetic protocols for the preparation of Au-Fe_3O_4 nanohybrid materials require harsh reaction conditions such as high temperature, additives, reducing agents and prolonged reaction time which decreases the environment /economic advantages of the strategy.[4] In view of the applications of magneto-plasmonics in diverse fields such as optics, imaging, sensing, solar cells, biomedicals and catalysis,[5] it is highly desirable to develop a rapid and convenient protocol for their preparation.

Recently, from our lab, we reported development of supramolecular assemblies based on derivative **1**.[6] These assemblies were then utilized as reactors and reductants for the preparation of Au-Fe_3O_4 NPs having size in the range of 4-8 nm at room temperature without using any additional reducing agent. Simultaneously, the aggregates of derivative **1** were themselves oxidized to polythiophene species which serves as stabilizer and shape-directing template for the assembly of Au- Fe_3O_4 NPs in an ordered fashion. The as prepared polythiophene Au-Fe_3O_4 nanohybrid materials exhibited remarkable catalytic efficiency in C(sp^2)−H bond activation of unprotected anilines under visible light irradiation to furnish synthetically versatile quinoline carboxylates. Previously, a variety of catalytic systems for C-H activation reaction have been reported which utilizes costly and non-recyclable organometallic/Ionic liquids as catalysts.[7] Furthermore, in most of these cases an inert atmosphere, prolonged heating at high temperature and use of toxic CO gas was needed for the preparation of quinolines through C-H activation reaction which basically reduced the environmental as well as economic benefits of the approach.[8] In comparison to these reports, derivative **1** supported Au-Fe_3O_4 NPs catalyzed the synthesis of quinolines with eco-friendly advantages (Table S1). We believe that polythiophene species facilitated the catalytic activity by absorbing visible radiations and transferring the energy to active metallic center which was evident from spectral overlap between the emission spectrum of polythiophene species and absorption spectrum of Au-Fe_3O_4 nanocomposites. We hypothesized that by increasing the emission intensity and wavelength, the extent of energy transfer from oxidized species to metallic centre can be increased, which will definitely improve the catalytic efficiency of the system. For increasing the energy transfer highly fluorescent materials emitting at longer wavelength are desirable. Recently, aggregation induced emission (AIE) phenomena is being explored for development of highly emissive thiolate derivatives which serve as supporting materials for gold nanoclusters.[9] These studies inspired us to examine the role of AIE active materials as the supporting material in enhancing the catalytic efficiency of the system. Hence, we planned the synthesis of hetero-oligophenylene derivative **6** having amino/thiophene

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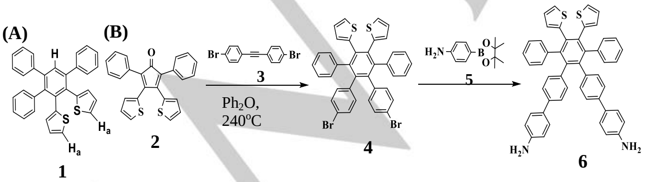
groups. We envisaged that the rotatable C-C bonds at the periphery may endow AIE characterstics to the synthesized derivative **6**. The amino/thiophene groups were incorporated in derivative **6** due to their known affinity for gold ions (Scheme 1). Gratifyingly, the derivative **6** exhibited AIE characterstics and formed fluorescent assemblies in the H_2O: THF solvent mixture which served as reactors to generate Au-Fe_3O_4 nanocomposites having size in the range of (1.5-2.0 nm). To the best of our knowledge, there is no report in literature regarding generation of Au-Fe_3O_4 nanocomposites having such a small size (Table S2). During the formation of Au-Fe_3O_4 NPs, assemblies of derivative **6** were oxidized to AIE active polymeric species **PTh-*co*-PANI-6** which showed broad emission in the broad range of 365-640 nm. A significant overlap between absorption spectra of Au-Fe_3O_4 NPs and emission spectra of the oxidized species was observed which indicated the possibility of good energy transfer between them. To check the validity of our hypothesis, we examined the model reaction between aniline **(10)** and methyl propiolate **(11)** in the presence of CO source in the presence of **PTh-*co*-PANI-6: Au-Fe_3O_4** NPs as catalyst. The reaction was complete in 5 hrs to furnish the desired product in 87% yield. In the presence of previously reported catalytic system, [6] the reaction was complete in 6 hrs to give the final product in 80% yield. This study validates our assumption that by making assemblies more emissive, increasing the emission intensity and wavelength of assemblies, extent of energy transfer and finally catalytic efficiency of the system can be enhanced. Further, **PTh-*co*-PANI-6: Au-Fe_3O_4** nanodots were deposited on a filter paper to prepare a “dip- catalyst”. The “dip- catalyst” serves as a reusable strip for carrying out the C(sp)–H activation and it showed recyclability up to 10 cycles. To the best of our knowledge, this is the first report regarding study of influence of structural features and photophysical properties of supporting materials on the photocatalytic efficiency of the system. Further, this is the first report of utilization of Au-Fe_3O_4 based ‘dip strip’ photocatalyst for the preparation of quinoline derivatives via C-H activation reaction.

Results and Discussion

Initially, precursor **4** was prepared *via* Diels-Alder reaction between derivatives **2**[10] and **3**. Further, precursor **4** and boronic ester **5** undergo Suzuki- Miyaura cross coupling reaction to deliver the target derivative **6** in 76% yield (Scheme 1). The structure of this derivative **6** was elucidated by different spectroscopic techniques (Figure S1).



Scheme 1. (A) Structure of derivative 1 and (B) Synthesis of derivative 6.

Afterwards, we analyzed the photophysical behavior of the compound in H_2O/THF solvent system. The UV-vis and temperature dependent absorption studies of derivative **6** in THF/H_2O solvent mixture suggested the development of *J*-aggregates (Figure S2-S3). In the emission studies, upon increasing the water content in the THF solutions (0-60%), a gradual increase in the intensity of the emission band was observed and the emission band was red shifted from 417 to 427 nm (Figure S4). The AIE behaviour of derivative **6** was further confirmed by viscosity dependent fluorescence studies (Figure S5). The formation of spherical aggregates of compound **6** was confirmed by TEM studies (Figure S6).

To ascertain the applicability of aggregates of derivative **6** for preparation of Au-Fe_3O_4 nanocomposites, we followed the procedure as reported earlier.[8] In the absorption studies, the simultaneous addition of Au^{3+} and Fe^{3+} ions (15 equiv.) to the solution of derivative **6**, SPR band of Au NPs appeared at 550 nm (after 25 mins) which was gradually shifted to 570 nm. The intensity of the level-off tail was also increased, thus, signifying the preparation of Au-Fe_3O_4 magnetic nanocomposites (Figure S7).[11] The color of the solution was also changed from colorless to yellow to purple and finally turned to reddish brown (Figure S8). The entire process was complete within 45 mins.

The TEM and HRTEM image of derivative **6** in the presence of Au^{3+} and Fe^{3+} ions (15 equiv.) revealed the existence of spherical **PTh-*co*-PANI-6: Au-Fe_3O_4** magnetic nanocomposites encapsulated into the network of polymeric species (Figure 1, S9). The DLS studies demonstrated the size of formed Au-Fe_3O_4 nanodots in the range of 1.5-2.0 nm (Figure S10). The powder XRD analysis of Au-Fe_3O_4 nanodots displayed diffraction peaks for *fcc* lattice of Fe_3O_4 NPs and Au NPs (Figure S11).[12] The XPS analysis of the **PTh-*co*-PANI-6: Au-Fe_3O_4** nanodots confirmed the presence of Au (0) (Au4f, 85.9 and 88.9 eV)and Fe^{3+} and Fe^{2+} species (Fe2p, 710.8 and 724.5 eV) in the **Au-Fe_3O_4** lattice.[13] Additionally, peaks were detected for S2p, C1s, O1s and N1s which were due to organic residue (Figure S12). The appearance of band at 630 cm^{-1} in the Raman spectrum relates to the A1g vibration mode of Fe_3O_4 NPs (Figure S13).[11] The DT-TGA analysis of **PTh-*co*-PANI-6: Au-Fe_3O_4** nanomaterials suggested a nonlinearly weight loss from 200 to 600 °C. From the measurements for weight loss, the amount of **PTh-*co*-PANI** coating layer on Au-Fe_3O_4 nanodots was found to be approximately 32% (Figure S14). From hysteresis measurements, the magnetic nature of **Au-Fe_3O_4** nanodots was estimated (Figure S15, Table S3).

During the formation of **Au-Fe_3O_4** nanodots the aggregates of derivative **6** were oxidized to **PTh-*co*-PANI**. To understand this process, a reaction was performed between derivative **6** (H_2O/THF) and Au^{3+} and Fe^{3+} ions at room temperature and after one hour, reaction mixture was left for slow evaporation at room temperature . The as formed magnetic Au-Fe_3O_4 nanodots were filtered and then washed with organic solvents ($CHCl_3$ and THF). The residue filtrate was allowed to evaporate to obtain the solid organic material and formed the oxidized species **PTh-*co*-PANI-6** (Figure 1).

As per ^1H NMR studies of the oxidized material (**PTh-*co*-PANI-6)**, the signals in the aromatic region were shifted and

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broadened which suggested the formation of polythiophene and polyaniline species **PTh-*co*-PANI-6** (Figure S16).[14] The ESI-MS spectrum exhibited peak at m/z = 2907.0722 which is in accordance with the theoretical molecular mass of polyaniline and polythiophene species $[C_{200}H_{138}N_8S_8H]^+$ (Figure S17). The powder XRD analysis of this sample showed the characteristic peaks suggesting the formation of polyaniline species[15] and polythiophene species (Figure S18).[16] The IR spectrum of the oxidized species also supported the formation of polythiophene and polyaniline species (Figure S19).[17] To check the porosity of the nanodots, the BET measurements were taken which detected the surface area of 34.46 m^2/g and pore volume 0.03 cm3/g.[18]

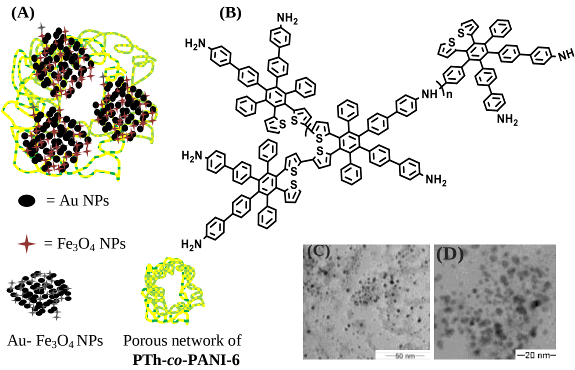
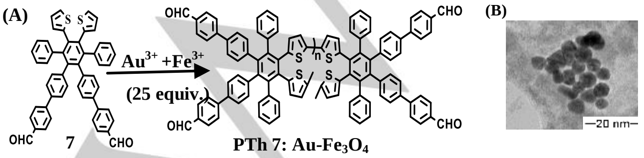


Figure 1. (A) Schematic representation of formation of **PTh-*co*-PANI-6** (B) Structure of polymeric species and TEM images of Au-Fe_3O_4 nanocomposites encapsulated into polymeric species with scale bars of (C) 50 nm (D) 20 nm.

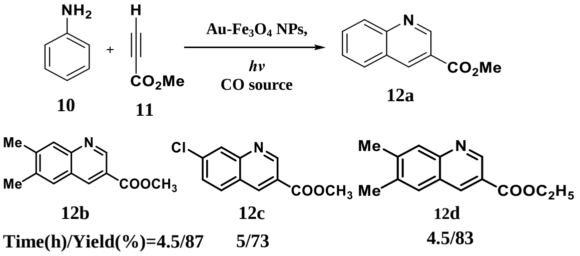
To get visualization into the influence of structural modifications on the size/shape of generated nanomaterials, we also synthesized derivative **7** having aldehyde groups (Scheme 2, Figure S20). Derivative **7** showed the AIE characteristics and served as reactors to generate **PTh- 7: Au-Fe_3O_4** nanocomposties (Figure S21-S22). The ^{1}H NMR and IR studies of the oxidized product showed the presence of aldehyde groups which suggested that aldehyde moieties are not involved in the reduction process (Figure S23). The TEM image also suggested the formation of **PTh- 7: Au-Fe_3O_4**. Interestingly, its size was found to be relatively large 20-30 nm from DLS studies (Figure S24). We believed that, oxidised species **PTh-*co*-PANI-6** due to the presence of higher number of binding sites (-NH_2/thiophene) could uniformly coat the as prepared nanohybrid materials and could restrict their growth as a result of which nanomaterials of smaller size are generated.



Scheme 2. (A) Schematic diagram (B) TEM image depicting the formation of polythiophene species **PTh 7: Au-Fe_3O_4** nanocomposites; (scale 20nm).

The emission spectrum of oxidised species **PTh-*co*-PANI-6** showed broad band in the region of 365 to 640 nm (λex=350 nm). The intensity of emission band of **PTh-*co*-PANI-6** was reduced (71%) when bare Au-Fe_3O_4 NPs (5 mol %) were added to this solution. This outcome clearly supported the possibility of energy transfer between oxidised species and metallic centre (Figure S25). To get insight into the photostability of the organic support, we exposed the solution of **PTh-*co*-PANI-6** in H_2O/THF (6:4) mixture to visible radiations under lab conditions. We recorded the emission spectra of **PTh-*co*-PANI-6** after 3 and 5 hrs and decrease in fluorescence intensity was observed (11% after 3 hrs, 55.6% after 5hrs) (Figure S26).

These studies encouraged us to explore the photocatalytic efficiency of the generated **Au-Fe_3O_4** nanocomposites in the C(sp^2)-H activation and C(sp)-N coupling reactions in the presence of visible light. The reaction between aniline **(10)** and methyl propiolate **(11)** was chosen as the model reaction. The reaction was performed using H_2O as a solvent, paraformaldehyde as CO source and **PTh-*co*-PANI-6: Au-Fe_3O_4** nanodots as the catalytic system (Scheme 3). The reaction was accomplished in 5 hrs to furnish target qunioline carboxylate derivative **(12a)** in 87% yield. Next, we performed the same reaction in the presence of **PTh-7: Au-Fe_3O_4** nanocomposites as the catalytic system. In this case, the reaction afforded the preferred product in 77% yield after 7 hrs. Under the optimized reaction parameters, the best yield i.e. 87% was obtained in the case of **PTh-*co*-PANI-6: Au-Fe_3O_4** nanodots which may be attributed to smaller size and porous morphology of the catalytic system (Table S4). Through these optimal reaction conditions, the scope of various substituted anilines and alkynes was examined using **PTh-*co*-PANI 6: Au-Fe_3O_4** as the catalytic system. To our delight, aryl amines bearing electron-rich **(-Me)**/ electron-withdrawing group (**-Cl**) and electron- deficient alkynes **(11)** all reacted well to afford the C−H activation products **(12a-d)** in moderate to excellent yields (Scheme 3).



Scheme 3. C(sp^2)-H activation reaction between aniline (10, 1 mmol), methyl propiolate (11, 1 mmol) and paraformaldehyde (2.5 mmol) catalyzed by **PTh-*co*-PANI-6** encapsulated Au-Fe_3O_4 nanocomposites under photocatalytic conditions (irradiation of 60 W tungsten filament bulb).

To explore the reaction mechanism of C(sp^2)-H activation reaction, the model reaction for C(sp^2)-H activation was performed in the presence of TEMPO, however, the reaction did not provide the desired product. Fortunately, we could isolate the ortho-adduct between aniline and TEMPO whose structure was confirmed by ^{1}H NMR spectra (Figure S27). The above studies clearly recommended that the generated radical species

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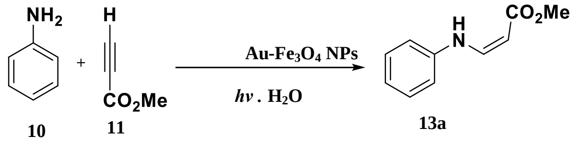
were essential for carrying out the C(sp^2)-H activation to yield quinoline carboxylates (Figure S28).

Next, we prepared ‘dip strip’ by dipping the filter paper into the solution of **PTh-*co*-PANI-6**: **Au-Fe_3O_4** nanodots. The SEM image of the filter paper indicates the coating of the paper strip by the nanomaterial (Figure S29). The ‘dip-strip’ catalyst was used for the model reaction between aniline **(10)** and methyl propiolate **(11)** under optimized parameters. The reaction was accomplished in 5 hrs to provide the desired product in 89% yield. The dip catalyst in the catalytic reaction was recovered and reused as such for the next reaction. After the 10th cycle, yield of target product decreased to 60% (Figure S30).

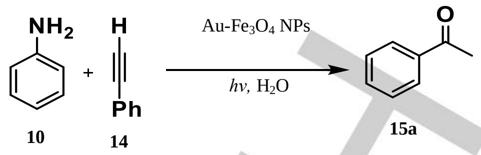
Further, we studied the catalytic activity of the **PTh-*co*-PANI-6: Au-Fe_3O_4** nanodots in the reaction between aniline and activated/ unactivated alkynes in the absence of CO source under photocatalytic conditions and at room temperature. The C(sp)-N coupling reaction between aniline (10) and methyl propiolate (11) in the absence of CO source was chosen as the model reaction (Scheme 4).



Scheme 4. C(sp)-N coupling reaction between aniline (10, 1 mmol), methyl propiolate (11, 1.2 mmol) catalyzed by **PTh-*co*-PANI-6: Au-Fe_3O_4** magnetic nanodots under photocatalytic conditions.

In this reaction, water was used as a sole reaction media in this C(sp)-N coupling reaction. Under the photcatalytic conditions, reaction was accomplished in 20 mins and afforded the β-amino acrylate derivative (13a) in 88% yield (entry 1, Table S5). Very instrestingly, when the same procedure was repeated at room temperature, it took 35 mins for completion. We examined the substrate scope of the reaction with regard to substituted anilines and alkynes at room temperature (Table S5). Under improved reaction parameters, substitution at both C2 and C4 positions of anilines was also well-tolerated (entry 2, Table S4). Notably, substrates having electron-donating/withdrawing groups at the C2 and C4 position with respect to amino group readily undergo the reaction (entries 3-6, Table S5). We also examined the recyclability of catalytic system in model reaction. Being magnetic catalyst it could be recycled and reused upto 13th cycle with continuous reduction in the reactivity of the catalyst. After the 13th cycle, the yield of the final product was decreased up to 52% (Figure S31).

On the other hand, the model reaction between aniline (10) and phenylacetylene (14) under photocatalytic conditions in the presence of **PTh-*co*-PANI-6: Au- Fe_3O_4** nanodots furnished the acetophenone (15a) (hydroamination reaction) as the product (Scheme 5).



Scheme 5. Hydroamination reaction between aniline (**10**, 1 mmol), phenyl acetylene (**14**, 1.2 mmol) catalyzed by **PTh-*co*-PANI-6** encapsulated **Au-Fe_3O_4** nanodots under photocatalytic conditions.

We also examined the reaction of –o/-m/-p substituted anilines with phenylacetylene and all of the substituted anilines on reaction with phenylacetylene yielded acetophenone (entries 2-5, Table S6). Interestingly, when the model reaction was executed without aniline the reaction did not yielded acetophenone (entry 2, Table S7). The model reaction was completely inhibited when performed in the absence of catalyst (entry 3, Table S7). We also checked the scope of substituted phenylacetylenes and the reaction proceeded faster with the electron rich phenylacetylene (entries 1-7, Table S6). The exclusive formation of desired Markovnikov type acetophenones may be accredited to the construction of a more stable imine and ability of the catalytic system to activate phenyl acetylene.

Conclusions

In conclusion, we have designed and synthesized AIE active and fluorescent aggregates of hetero-oligophenylene derivative 6 which served as reactors for the formation of **PTh-*co*-PANI-6: Au-Fe_3O_4** nanocomposites. The supramolecular porous ensemble **PTh-*co*-PANI-6: Au-Fe_3O_4** served as an effective and recyclable catalytic system for C(sp^2)−H bond activation under smooth and eco-friendly conditions. Further, **PTh-co-PANI-6: Au-Fe_3O_4** nanocomposites were deposited on a filter paper to prepare a “dip-strip” which served as a reusable strip (upto 10 cycles) for carrying out the C-C/C-N bond formation reaction.The work being presented in the manuscript demonstrate the important role of AIE active supporting material in enhancing the efficiency of Au-Fe_3O_4 based photo catalytic system.

Acknowledgements

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Keywords: AIE active hetero-oligophenylenes • Supramolecular porous ensemble • Au-Fe_3O_4 nanodots • Recyclable ‘dip catalyst’ • C(sp^2)−H bond activation.

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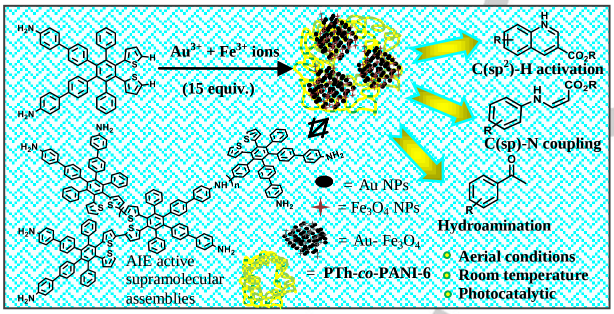
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

The as prepared AIE active supramolecular ensemble could harvest ambient visible light and can be utilized as efficient and recyclable "dip strip" photocatalyst for C(sp^2)−H bond activation for the construction of quinoline carboxylates *via* C−H activation.

Harpreet Kaur, [‡] *Mandeep Kaur,* [‡] *Preet Kamal Walia,* [‡] *Manoj Kumar and Vandana Bhalla*



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