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ARTICLE

Supramolecular ensemble of PBI derivative and Cu_2O NPs: Potential photo catalysts for Suzuki and Suzuki type coupling reactions

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Aggregates of PBI derivative **1** in combination with Benedict's reagent have been used for the first time as reactors for facile preparation of Cu_2O NPs at room temperature. During this process aldehyde groups of aggregates of derivative **1** are oxidized to carboxylate groups which act as stabilizers for Cu_2O NPs to generate supramolecular ensemble **2**:Cu_2O. Interestingly, the *in situ* generated supramolecular ensemble (**2**:Cu_2O) of Cu_2O NPs and aggregates of oxidized species **2** exhibited excellent photocatalytic efficiency in Suzuki-Miyaura and Suzuki type cross-coupling reactions under mild and eco-friendly conditions.

Introduction

Suzuki-Miyaura coupling between organohalides and organoboronic esters/acids is one of the most powerful synthetic methods for the preparation of synthetic building blocks of various natural products and biologically important compounds.[1] Under conventional conditions, palladium based catalytic systems due to their high stability and remarkable efficiency are most preferred choice to carry out Suzuki coupling reactions.[2] Interestingly, pursuit of organic chemists towards making the Suzuki reaction 'green' is a continuous process and as a result of this a variety of new approaches have been developed to carry out the Suzuki reaction under eco-friendly conditions.[3] In this direction, a variety of catalytic systems have been developed which harvest clean, abundant and economical solar energy to carry out Suzuki coupling.[4] However, the use of costly and toxic palladium as major component of these catalytic systems actually decreased the environmental and economical advantage of the strategy.[5] Very recently, we developed an *in situ* generated Ag@Cu_2O core-shell nanomaterials which harvested the visible light to catalyze Suzuki-Miyaura and Suzuki type coupling reactions under mild conditions.[6] The coating of plasmonic silver nanoparticles (AgNPs) with semiconductor Cu_2O NPs served dual purpose, first, the photocatalytic activity of plasmonic system was enhanced. Second, by coating expensive metal NPs with inexpensive material, we were successful in reducing the cost of the photocatalytic system. In continuation of our efforts in this direction, we were then interested in the development of a supramolecular photocatalytic system having dye stabilized semiconductor nanomaterial for carrying out Suzuki and Suzuki type coupling reactions. In this type of system, the semiconductor material and molecules of dye serve as antenna and absorb the visible radiations to get excited. Eventually, the excited species activate the substrate molecules to facilitate the organic reactions.[7] Cu_2O is our choice as semiconductor nanomaterial as it is economical, abundant and stable p-type semiconductor which has been used as an efficient catalyst for C-C, C-N and C-O bond formation reactions.[8] Perylene bisimide (PBI) is a scaffold of our choice as dye stuff due to its high fluorescence quantum yield, high photostability. In addition, PBI derivatives are also reported for their role as light harvesting antenna.[9] Recently, we developed aggregates of PBI derivative **1** (Fig. 2) having aldehyde groups and utilized these aggregates for preparation of AgNPs.[10] Derivative **1** was found to be very stable and did not exhibit any decomposition in solid as well as solution phase even upon month long exposure to room light and air. Furthermore, the absorption spectrum of derivative **1** in H_2O/THF (1:1) covers the whole visible region. Thus, we decided to use aggregates of derivative **1** having aldehyde groups at the periphery as dye molecule in our designed photocatalytic system. Further, we envisioned that aldehyde groups of derivative **1** in combination with Benedict's reagent could reduce cupric ion to copper NPs which under aerial conditions will be oxidised to cuprous oxide NPs. We envisaged that during this process aldehyde groups of derivative **1** will be oxidized to carboxylate groups which will stabilize the *in situ* generated Cu_2O NPs to generate a supramolecular photocatalytic ensemble. As expected, aggregates of derivative **1** in the presence of Benedict's reagent served as reactors for the generation of Cu_2O NPs. Interestingly, the *in situ* generated supramolecular ensemble (**2**:Cu_2O) of Cu_2O NPs and aggregates of oxidized species of derivative **1** served as

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efficient photocatalytic system for carrying out Suzuki-Miyaura cross coupling and Suzuki type coupling reactions under mild (visible light radiation, EtOH/H_2O solvent system and room temperature) and ecofriendly conditions. The work being presented here has several advantages; 1) for the first time aggregates of PBI derivative **1** in combination with Benedict's reagent have been used for facile preparation of Cu_2O NPs at room temperature. Various methods using wet chemistry techniques have been used for the development of Cu_2O NPs. However, these methods suffer from the limitations of requiring longer reaction time, high temperature, reducing agents and additives.[11] In comparison, the method being reported in the present manuscript is a convenient method for the preparation of stable Cu_2O NPs under mild conditions (Table S1, ESI†). 2) for the first time supramolecular ensemble of semiconductor Cu_2O NPs and PBI derivative have been used as efficient and recyclable photocatalysts for Suzuki-Miyaura cross-coupling reactions of aryl halides with aryl boronic acid esters in environmentally benign solvent mixture under aerial conditions at room temperature. In comparison, the photocatalytic performance of supramolecular photocatalytic ensemble **2**:Cu_2O is better than the reported photocatalytic systems for Suzuki-Miyaura cross-coupling reaction (Table S2, ESI†). 3) the supramolecular ensemble **2**:Cu_2O also exhibited high catalytic efficiency in Suzuki-type cross-coupling reactions of N-tosylaziridine with different types of organoborons under aerial conditions.

Results and Discussion

Perylene bisimide derivative **1** was synthesized by reported method.[10] It formed aggregates in mixed aqueous media and TEM image of the derivative **1** (1 mM) in H_2O/THF (1:1) solution shows the presence of irregular shaped aggregates (Fig. S1, ESI†). The addition of incremental amounts of derivative **1** (1 mM) dissolved in H_2O/THF (1:1) solvent mixture into the solution of Benedict's reagent (0.04 M) generated the Cu_2O NPs. The whole process was accompanied by apparent color change from blue to yellowish green (Fig. 1).

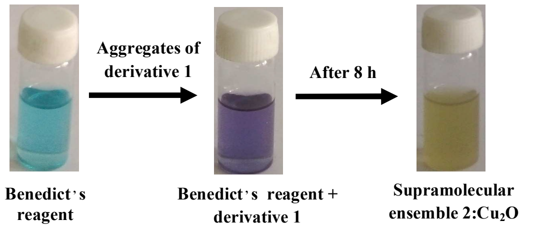

Fig. 1: Schematic diagram for the formation of supramolecular ensemble 2:Cu_2O from Benedict's solution on addition of derivative 1.

The UV-vis absorption spectra of derivative **1** in H_2O/THF (1:1) in presence of aqueous solution of Benedict's reagent exhibited a broad absorption band at 690 nm corresponding to Cu_2O NPs after 8 h.[12] Furthermore, from UV-vis studies, it is clear that in absence of derivative **1**, no band corresponding to NPs is formed which highlights the importance of aggregates of derivative **1** in generation of supramolecular ensemble **2**:Cu_2O (Fig. 2).

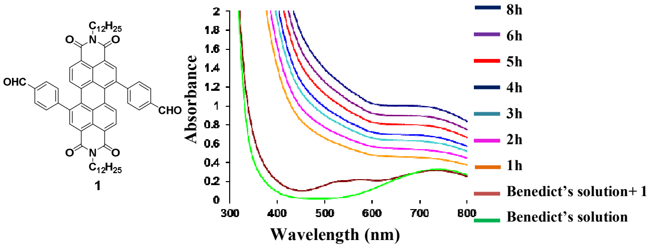

Fig. 2: UV-vis spectra of aqueous solution of supramolecular ensemble **2**:Cu_2O, Benedict's solution in the presence and absence of derivative **1**; UV-vis band at 690 nm correspond to supramolecular ensemble **2**:Cu_2O.

The fluorescence spectrum of derivative **1** in H_2O/THF (1:1) shows an emission band at 590 nm. Upon addition of Benedict's reagent (350 µL, 0.04 M), 76% quenching of the emission band is observed (Fig. S2, ESI†). High-resolution TEM (HR-TEM) images of aqueous Benedict's solution in the presence of aggregates of derivative **1** showed the presence of spherical NPs (Fig. 3). The particle size distribution of these NPs is shown in Fig. 3C. The lattice fringes showed *d*-spacing of 247.89 pm corresponding to the (111) planes of Cu_2O. The average size of Cu_2O NPs was found to be 8-10 nm. The powder XRD diffraction pattern of these NPs showed the reflection peaks of Cu_2O NPs (Fig. S3, ESI†).[13] We also examined the effect of amount of aggregates of derivative **1** on shape and size of generated NPs. When ratio of aggregates of derivative **1** to Benedict's reagent was changed from 1:1 to 2:1, spherical Cu_2O NPs of almost same size (8-10 nm) were observed while on switching this ratio to 1:2, an increase in the size of Cu_2O NPs (10-15 nm) was observed (Fig. S4, ESI†).

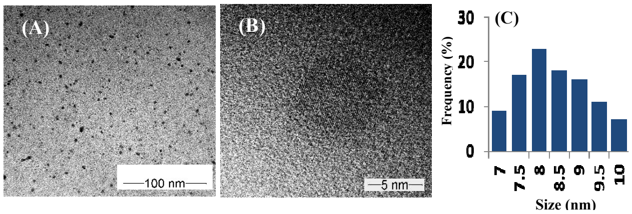

Fig. 3: (A) TEM image of spherical supramolecular ensemble 2:Cu_2O; (B) HRTEM image of generated supramolecular ensemble 2:Cu_2O Scale bar (A) 100 nm and (B) 5 nm (C) Particle size distribution of TEM image (A).

We believe that in the presence of high amount of Benedict's reagent, the number of reduced copper ions is increased, thus, Cu_2O nanoparticles of slightly bigger size were obtained. Thus, by changing the amount of aggregates of derivative **1,** size of Cu_2O NPs could be controlled; however, shape of generated NPs remained same. We then slowly evaporated the solution of aggregates of derivative **1** containing Cu_2O NPs. The precipitates were observed after 2 days which were filtered and washed with $CHCl_3$ and THF. The ^1H NMR spectrum of the residue so obtained after evaporation of the solvent showed upfield shift of the aromatic protons and no peak corresponding to aldehyde protons. (Fig. S5, ESI†). The FTIR studies of the residue showed the absence of the band corresponding to aldehyde groups and presence of two new bands at 1600 and 1400 cm^{-1} corresponding to carboxylate groups.[14] Further, the absorption band corresponding to Cu(I)-O vibration appeared at 625 cm^{-1} (Fig. S6, ESI†). The ^1H NMR

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and IR studies suggest the oxidation of aldehyde groups to the carboxylate groups during the formation of Cu_2O NPs.

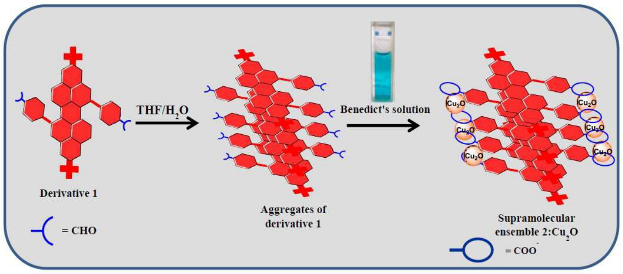


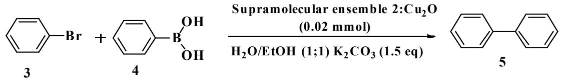
Fig. 4: Schematic diagram showed the formation of supramolecular ensemble $2{:}Cu_2O$.

The fluorescence spectrum of oxidized species of derivative **1** (10 μM) in H_2O/THF (1:1) solvent mixture exhibited an emission band at 600 nm. Upon addition of aqueous dispersion of Cu_2O NPs (300 μL, 0.04 M) to this solution, 83% quenching of the emission was observed due to the energy transfer from oxidized species of PBI derivative **1** to Cu_2O NPs (Fig. S7 in ESI†). We also carried out time resolved fluorescence studies of oxidized species of derivative **1** in the absence and presence of aqueous dispersion of Cu_2O NPs. The solution of oxidized species in H_2O/THF (1:1) showed average decay time of 7.12 ns, however, in presence of Cu_2O NPs (300 μL, 0.04 M) the average decay time decreased to 2.87 ns (Fig. S8, ESI†). Furthermore, a strong overlap was observed between emission spectrum of oxidized species of derivative **1** and absorption spectrum of Cu_2O NPs (Fig. S9 in ESI†). All the above studies support the energy transfer from oxidized species of PBI derivative **1** to Cu_2O NPs.[9,15] On the basis of these studies, we believe that aggregates of derivative **1** in combination with Benedict's reagent reduce the copper ions to Cu_2O NPs and during this process the aldehyde groups of derivative **1** get oxidized to carboxyl groups. Further, aggregates of oxidized species of derivative **1** acted as stabilizers to generate supramolecular ensemble **2**:Cu_2O (Fig. 4).[16]

To understand the role of oxidized species of derivative **1** in the preparation of Cu_2O NPs. We carried out UV-vis studies of Benedict's solution in the presence of oxidized species of derivative **1**. Upon addition of oxidized species to Benedict's solution, no band corresponding to Cu_2O NPs was observed (Fig. S10 in ESI†). On the basis of these studies, we believe that oxidized species play no role in generation of Cu_2O NPs.

Since copper containing compounds are known as co-catalyst in C-C bond formation reactions,[17] we planned to investigate the catalytic efficiency of *in situ* generated supramolecular ensemble **2**:Cu_2O in the Suzuki-Miyaura coupling reactions. We began with Suzuki-Miyaura cross coupling reaction between bromobenzene and phenyl boronic acid as the model reaction under thermal conditions. The reaction went smoothly in the presence of supramolecular ensemble **2**:Cu_2O (0.02 mmol) in THF as well as in H_2O/EtOH (1:1) solvent mixture (Table 1, entries 1 and 2). The reaction between bromobenzene and phenyl boronic acid in presence of supramolecular ensemble **2**:Cu_2O under aerial conditions also moved smoothly to furnish the desired product in 68% yield (Table 1, entry 3). The above studies show the catalytic efficiency of supramolecular ensemble **2**:Cu_2O in the Suzuki coupling reaction. Further, we planned to carry out the model reaction under photocatalytic condition. For this, we carried out the reaction of bromobenzene and phenyl boronic acid in the presence of supramolecular ensemble **2**:Cu_2O in a H_2O/EtOH (1:1) solvent mixture under visible light irradiation. A 100 W tungsten filament bulb was used as the irradiation source and to avoid the photo-heating effect the reaction vial was submerged in a water bath. The reaction was complete in 8 h and the desired product was obtained in 73 % yield (Table1, entry 4). Interestingly, when same reaction was carried out in THF, the desired product was obtained in 40% yield (Table 1, entry 5). We believe that electron transfer is suppressed in aprotic solvent which decreases the yield of the desired product.[18] The same reaction when carried out in the absence of K_2CO_3 furnished no product (Table 1, entry 6), hence, basic medium is a prerequisite for carrying out Suzuki reactions. We also carried out the model reactions under dark conditions; however, the reaction did not proceed to furnish the desired product (Table 1, entry 7).

Table 1: Screening of the photocatalytic Suzuki coupling reaction of bromobenzene and phenyl boronic acid using supramolecular ensemble $2{:}Cu_2O$ as the photocatalyst.



Entry	Catalyst	Reaction conditions	Base	Time	Yield
1	Supramolecular ensemble $2{:}Cu_2O$NPs	THF, heating (80–90 ^{O}C), N_2 atm	K_2CO_3	14 h	75%
2	Supramolecular ensemble $2{:}Cu_2O$NPs	H_2O/EtOH, heating (80-90 ^{O}C), N_2 atm	K_2CO_3	14 h	77%
3	Supramolecular ensemble $2{:}Cu_2O$NPs	H_2O/EtOH, heating (80–90 ^{O}C), Air	K_2CO_3	14 h	68%
4	Supramolecular ensemble $2{:}Cu_2O$NPs	H_2O/EtOH, visible light	K_2CO_3	8 h	73%
5	Supramolecular ensemble $2{:}Cu_2O$NPs	THF, visible light	K_2CO_3	8 h	40%
6	Supramolecular ensemble $2{:}Cu_2O$NPs	H_2O/EtOH,visible light	-	8 h	-
7	Supramolecular ensemble $2{:}Cu_2O$NPs	H_2O/EtOH, dark	K_2CO_3	8 h	-
8	Aggregates of derivative **1**	H_2O/EtOH,visible light	K_2CO_3	8 h	-
9	Oxidized species **2**	H_2O/EtOH,visible light	K_2CO_3	8 h	-
10	Bare Cu_2ONPs (Ref. 12a)	H_2O/EtOH,visible light	K_2CO_3	12 h	35%
11	Bare Cu_2ONPs (Ref. 12a) + aggregates of derivative **1**	H_2O/EtOH,visible light	K_2CO_3	8 h	36%
12	Bare Cu_2ONPs (Ref. 12a) + oxidized species **2**	H_2O/EtOH,visible light	K_2CO_3	8 h	70%

Furthermore, we carried out the model reaction in presence of aggregates of derivative **1** and oxidized species of derivative **1**

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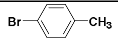
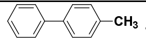
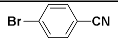
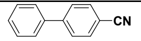
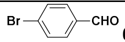
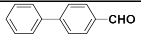
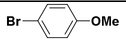
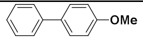
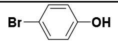
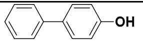
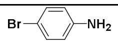
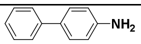
without using Cu_2O NPs (Table 1, entries 8 and 9). The oxidized species of derivative **1** (compound **2**) was prepared by the oxidation reaction of derivative **1** with 2 equiv of 70% ^{t}BuOOH in acetonitrile (pS5, ESI†). As expected none of these reactions furnished the desired product. To understand the role of aggregates of derivative **1**/oxidized species of derivative **1** in the photocatalytic efficiency of NPs, we prepared bare Cu_2O NPs by reported method[12a] and carried out model reaction using these NPs. The reaction was complete in 12 h and the desired product was obtained in 35% yield (Table 1, entry 10). In the next part of our work, we carried out the model reaction in the presence of bare Cu_2O NPs and aggregates of derivative **1** and the desired product was obtained in 36% yield (Table 1, entry 11). We also carried out model reaction in presence of bare Cu_2O NPs and oxidized species of derivative **1** (residue obtained after evaporating the solution of *in situ* generated NPs). The reaction was complete in 8 h and the desired product was obtained in 70% yield (Table 1, entry 12). We believe that aggregates of oxidized species of derivative **1** assisted the Cu_2O NPs in harvesting visible radiations more efficiently. On the basis of above studies, we conclude that aggregates of oxidized species of derivative **1** influence the photocatalytic efficiency of the system and are important for stabilization of generated NPs.

To check the scope of substrates, we utilized the *in situ* generated supramolecular ensemble **2**:Cu_2O as a photocatalyst in coupling of different types of aryl halides (having electron donating and withdrawing groups) with phenyl boronic acid to afford the desired products in moderate to excellent yields (Table 2). Further, the present set of reaction conditions are tolerant to diverse functional groups such as aldehyde, hydroxyl and nitrile (Table 2).

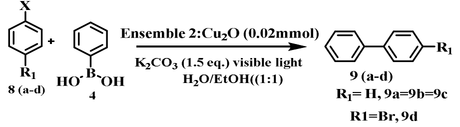
Table 2: Supramolecular ensemble **2**:Cu_2O catalyzed photocatalytic Suzuki type coupling reactions between various bromo derivatives and phenyl boronic acid

Entry	Aryl bromo derivatives	Product	Yield (%)
1	 **6a**	 **7a**	76
2	 **6b**	 **7b**	65
3	 **6c**	 **7c**	67
4	 **6d**	 **7d**	79
5	 **6e**	 **7e**	70
6	 **6f**	 **7f**	78

Reaction conditions: (a) Phenyl boronic acid (1 equiv.); (b) Supramolecular ensemble 2:Cu_2O NPs (0.02mmol); (c) K_2CO_3 (1.5 equiv.); RT.

To check the scope of substrates, we carried out photocatalytic Suzuki coupling of aryl halides with phenyl boronic acid in the presence of *in-situ* generated supramolecular ensemble **2**:Cu_2O which afforded desired products in moderate to excellent yields (Table 3). In the presence of *in situ* generated supramolecular ensemble **2**:Cu_2O NPs, 1-bromo-4-iodobenzene reacted with phenyl boronic acid to furnish 4-aryl-1-bromobenzene (Table 3). This study shows the high selectivity of *in situ* generated supramolecular ensemble **2**:Cu_2O in Suzuki coupling.

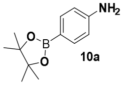
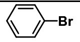
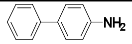
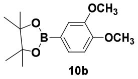
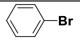
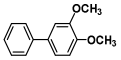
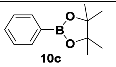
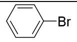
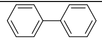
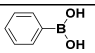
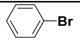
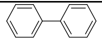
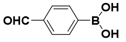
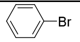
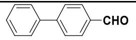
Table 3: supramolecular ensemble 2:Cu_2O catalyzed photocatalytic Suzuki coupling reactions between various aryl halides and phenyl boronic acid.



Entry	Reactant	Product	Time	Yield (%)
1	**8a**;X=Cl,R=H	**5 = 9a**;R_1=H	24 h	48%
2	**8b**;X=Br,R=H	**5 = 9b**;R_1=H	8 h	73%
3	**8c**;X=I,R=H	**5 = 9c**;R_1=H	4.3 h	81%
4	**8d**;X=I,R=Br	**9d**;R_1=Br	5 h	80%

We further checked the scope of the coupling by carrying out the reaction of bromobenzene with different types of boronic acids having electron rich and withdrawing groups as substituents using supramolecular ensemble **2**:Cu_2O as photocatalyst and results are given in Table 4. It is clear from these results that higher yields are obtained in the case of boronic acids/esters having electron rich substituents (Table 4, entries 1 and 2). Further, photocatalytic Suzuki coupling of phenyl boronic ester with bromobenzene furnished desired product in 72% yield indicating no effect of boronic acid or ester groups on this reaction.

Table 4: supramolecular ensemble **2**:Cu_2O catalyzed photocatalytic Suzuki coupling reactions between bromobenzene and various boronic acids/esters.

Entry	Bornic ester/acid used	Substrate	Product	Yield
1	 **10a**	 **3**	 **7f**	75%
2	 **10b**	 **3**	 **11c**	77%
3	 **10c**	 **3**	 **5**	72%
4	 **10d**	 **3**	 **5**	73 %
5	 **10e**	 **3**	 **7c**	65 %

Reaction conditions: (a) Phenyl boronic acid (1 equiv.); (b) Supramolecular ensemble **2**:Cu_2O NPs (0.02mmol); (c) K_2CO_3 (1.5 equiv.); RT.

All the products were isolated and characterized by ^{1}H NMR spectroscopy (PS14-PS22, ESI†). We carried out the Suzuki coupling of bromobenzene with phenyl boronic acid in a H_2O/EtOH (1:1) solvent mixture to examine the catalytic efficiency of catalyst. When the quantity of supramolecular ensemble **2**:Cu_2O is 0.02 mmol the yield is 75% in 8 h. However, the yield of desired product remains quantitative (68 %) upon decrease of supramolecular ensemble **2**:Cu_2O loading from 0.02 to 0.005 mmol (Table S4, ESI†) and no product was obtained when same reaction is carried out without catalyst.

The recyclability of catalyst is a key factor from environment and synthetic point of view. The reaction between

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bromobenzene and phenyl bornic acid was chosen as the model reaction to study the recyclability of the catalyst.

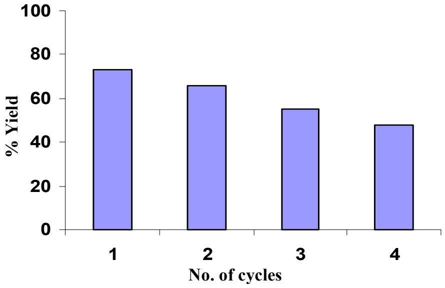
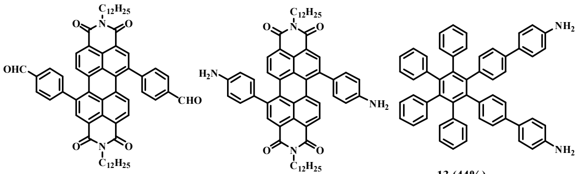


Fig. 5: Recyclability of supramolecular ensemble **2**:Cu_2O catalyst for Suzuki coupling reaction.

After complete conversion, the solvent was evaporated and product was extracted using dichloromethane. The residue containing supramolecular ensemble **2**:Cu_2O catalyst was subjected to the next run of the Suzuki reaction by charging with the same substrate molecules. The supramolecular ensemble **2**:Cu_2O could be recycled as a catalyst at least 4 times with a decrease in the activity (Fig. 5). We believe that due to the continuous photoexcitation of catalyst, Cu_2O NPs get deactivated due to photocorrosion and thus the catalytic efficiency of supramolecular ensemble decreased.[19] After the catalytic reactions, the TEM images of recycled supramolecular ensemble **2**:Cu_2O revealed no change in its size and morphology (Fig. S11, ESI†). We also carried out atomic absorption studies (AAS) of the residual liquid left after the recycling of the catalyst and found that only 0.012 ppm of Cu had leached into the solution (pS13 in ESI†).

To evaluate the versatility of *in situ* generated supramolecular ensemble **2**:Cu_2O, we planned to evaluate its catalytic efficiency in the reaction involving preparation of perylenedimide (PBI) derivatives **1** and **12** (Fig. 6). Under photocatalytic conditions, derivatives **1** and **12** were obtained in 47% and 48% yields, respectively (PS23-PS25, ESI†). Earlier, we have reported synthesis of derivative **1** and 12[20] under palladium catalyzed thermal conditions in 50% and 78%, respectively. We also utilized the *in situ* generated supramolecular ensemble **2**:Cu_2O as photocatalyst for preparation of electron rich hexaphenylbenzene derivative **13** and the desired product was obtained in 44% yield (Fig. 6). Earlier, the synthesis of HPB is reported in 55% yield by carrying out Suzuki reaction in THF solvent in the present of Pd^{2+} catalyst.[21] These studies highlight the practical applicability of supramolecular ensemble **2**:Cu_2O in Suzuki coupling reactions.



1 (47%)
12 (48%)
13 (44%)

Fig. 6: Practical applicability of supramolecular ensemble **2**:Cu_2O in the synthesis of PBI and HBC derivatives by Suzuki coupling reactions.

To get insight into the mechanism of supramolecular ensemble **2**:Cu_2O photocatalyzed Suzuki coupling reaction, we carried out reaction between bromobenzene and phenyl boronic acid in the presence of a hole scavenger (10%, triethanolamine (TEOA) and the desired product was obtained in 34% yield. We also carried out the same reaction in the presence of benzoquinone as a radical scavenger and the desired product was obtained in 35% yield. However, when both the scavengers were used together the target compound was obtained in 12% yield. These studies suggest that photogenerated hole and electron pair are essential for carrying out the Suzuki coupling reactions. However, when the photo-generated electron-hole pair is blocked, the supramolecular ensemble **2**:Cu_2O electron pair still remain active to catalyse the coupling reaction with one activated aryl species but in lower yield. We believe that electron-hole pair is generated within the supramolecular ensemble **2**:Cu_2O upon light irradiation. The photoexcited electrons activate the C-X bond of aryl halide and breaking of the C-X bond is the rate determining step. Further, our previous investigation suggests that the active substrates such as iodobenzene, bromobenzene and aryl halides having electron rich substituents furnished the desired products in higher yields. These findings also support our corresponding results of cleavage of C-X bond in the rate determining step. Taking account of all these observations, we propose that the holes inside the phocatalysts activates the C-B bond of phenylboronic acid in basic medium to transform the boronic acid into electronically negative $B(OH)_3$ species. Afterwards, reductive elimination and transmetalation are followed which lead to the formation of the desired product. A plausible mechanism is proposed for the Cu_2O NPs catalyzed photocatalytic Suzuki cross-coupling reaction (Fig. 7).

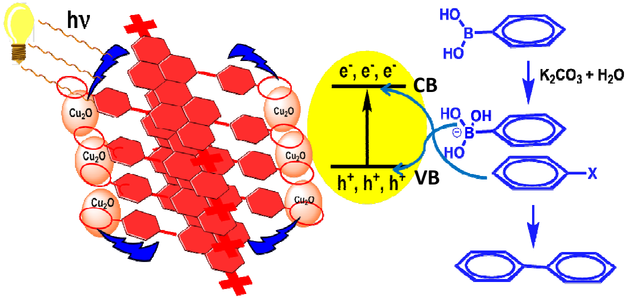


Fig. 7: Proposed photocatalytic mechanism of Suzuki cross-coupling reaction.

Having done all this, we planned to examine the photocatalytic efficiency of *in situ* generated supramolecular ensemble **2**:Cu_2O in the ring opening reactions of N-tosylaziridine to obtain phenylethylamine. Derivatives having phenylethylamine motifs are important due to their extensive use in synthesis of drug targets for the treatment of various diseases.[22] Traditionally, synthesis of these compounds *via* ring opening reaction of aziridines requires strong organometallic nucleophiles.[23] In the present investigation, we carried out the reactions between N-tosylaziridine and different type of boronic acids/esters in the presence of *in situ* generated supramolecular ensemble **2**:Cu_2O by using K_2CO_3 as the base in H_2O/EtOH (1:1) under aerial conditions. All the reactions went

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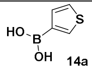
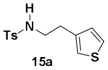
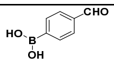
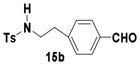
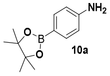
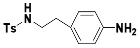
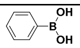
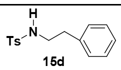
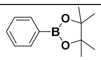
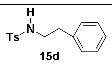
smoothly and desired products were obtained in good to excellent yields. The results are summarized in Table 5 which clearly show that electron rich boronic acids/esters yielded the desired products in higher yields (PS26-PS29, ESI†).

Table 5: Supramolecular ensemble **2:**Cu_2ONPs catalyzed photocatalytic Suzuki type Coupling reactions between different boronic acid/ester and tosyl aziridine.

Entry	Bornic ester/acid used	Product	Time	Yield
1	 14a	 15a	6 h	70%
2	 14b	 15b	8h	60%
3	 10a	 15c	4h	83%
4	 4	 15d	5 h	79%
5	 10e	 15d	5 h	77%

Reaction conditions: a) Aziridine (1 equiv.); b) Boronic acid/ester (1 equiv.); c) Supramolecular ensemble 2:Cu_2O NPs (0.02 mmol), RT.

Conclusion

In conclusion, aggregates of derivative **1** in combination with Benedict's reagent have been used for *in situ* generation of supramolecular ensemble **2**:Cu_2O NPs. The supramolecular ensemble **2**:Cu_2O NPs served as efficient photocatalysts in Suzuki-Miyaura and Suzuki type cross coupling reactions under mild and environmental friendly conditions. In contrast to the conventional systems, this catalytic system is economically, easy to prepare, recyclable and ecofriendly.

Experimental Section

General Experimental Procedures

Instrumentations

UV-vis spectra of synthesized compounds were performed in THF and H_2O/THF mixture by using SHIMADZU UV-2450 spectrophotometer having a quartz cuvette (path length, 1 cm). High Resolution Transmission Electron Microscope (HR-TEM) images were recorded on a TEM-JEOL 2100F. FTIR spectrum was recorded on Varian 660-IR spectrometer. Photocatalytic experiments were carried out by using the 100 W tungsten filament bulb as an irradiation source. The ^1H and ^{13}C NMR spectra were recorded on a JEOL-FT NMR-AL 300 MHz and Bruker-FT NMR-AL 500 MHz spectrophotometers using $CDCl_3$ and DMSO-d_6 as solvent and tetramethylsilane ($SiMe_4$) as internal standards. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad, m = multiplet), coupling constants J (Hz), integration and interpretation.

Preparation of stock solution of Benedict's reagent

1 M stock solution of Benedict's reagent was prepared by dissolving 10 g of sodium carbonate and 17.3 g of sodium citrate dihydrate in 85 mL of distilled water. Then, 1.73 g copper sulfate pentahydrate dissolved in 10 mL of water was added to the above solution and further diluted to make the total volume 100 mL. Then, 0.04 M of this solution was used for the preparation of supramolecular ensemble **2**:Cu_2O.

Preparation of supramolecular ensemble 2:Cu_2O

To a 2 mL solution of aggregates of derivative **1** (1 mM) was added 1 mL Benedict's solution (0.04 M). The colour of solution changed from blue to purple immediately. After continuous stirring for 8 h, the colour of the mixture further changed from purple to yellowish green indicating the formation of supramolecular ensemble **2**:Cu_2O of oxidized species of derivative **1** (**2**) and Cu_2O NPs. The resulting solution was sonicated to get homogeneous mixture and was used as such in the photocatalytic experiments.

General experimental procedure for photocatalytic Suzuki-Miyaura coupling reaction:

Phenyl boronic acid (0.318 mmol, 0.038 g), K_2CO_3 (0.477 mmol, 0.066 g) was added to the stirred solution of supramolecular ensemble **2**:Cu_2O (0.020 mmol) in H_2O/EtOH (1:1) mixture. Aryl halide (0.318 mmol, 0.05 g) was then added to the reaction mixture and degassed with vacuum pump for 3 min. The reaction mixture was then irradiated with a 100 W tungsten filament bulb (0.4 W/cm^2) to provide visible light for 8 h. To prevent the heating effect the reaction vial was put in water bath to maintain the room temperature. After completion of the reaction, solvent was removed under reduced pressure and the residue so obtained was extracted with dichloromethane (3×20 mL). The combined organic layer was then washed with water, dried over anhydrous Na_2SO_4 and distilled under reduced pressure to obtain a crude product which was recrystallized from dichloromethane and hexane solvent mixture to get pure product.

General experimental procedure for photocatalytic Suzuki type cross-coupling reaction:

To a 50 mL round bottom Flask (RBF) were added *N*-tosyl-aziridine (0.253 mmol, 0.05 g), phenylboronic acid (0.253 mmol, 0.03 g), K_2CO_3 (0.380 mmol, 0.053 g) and 0.02 mmol of supramolecular ensemble **2**:Cu_2O in H_2O/EtOH (1:1) mixture. The resulting mixture was degassed under reduced pressure for 3 min. and then irradiated from a distance of 10 cm with a 100 W tungsten filament bulb (0.4 W/cm^2) to provide visible light for 5 h. To prevent the heating effect the reaction vial was put in water bath to maintain the room temperature. After completion of the reaction, solvent was evaporated under vacuum pump and residue so obtained was extracted with dichloromethane (3×20 mL). The combined organic layer was then washed with water, dried over anhydrous Na_2SO_4 and distilled under reduced pressure to obtain a crude product which was recrystallized from dichloromethane and hexane solvent mixture to get pure product.

Characterization

(5)[24] ^1H NMR (300 MHz, $CDCl_3$): δ = 7.6 [d, 4H, J = 6.9 Hz, ArH], 7.44 [t, 4H, J = 7.3 Hz, ArH], 7.36 [d, 2H, J = 7.5 Hz, ArH].

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(7a)[25]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.70 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.50-7.46 (m, 2H), 7.40-7.43 (m, 1H), 7.32-7.39 (m, 2H), 2.02 (s, 3H).

(7b)[26]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.31-7.37 (m, 1H).

(7c)[26]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.81 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 7.5 Hz, 2H), 7.22-7.30 (m, 3H).

(7d)[26]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (t, *J* = 8.85 Hz, 4H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.35 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H).

(7e)[26]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.35 Hz, 2H), 7.34 (t, *J* = 7.35 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.77 (s, 1H).

(7f)[26]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 4H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 2H), 4.67 (s, 2H).

(9d)[25]: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35 [d, 2H, J = 8.5 Hz, ArH], 7.34 [d, 2H, J = 8.5 Hz, ArH], 7.11 [t, 2H, J = 9.3 ArH], 7.00-7.04 [m, 3H, ArH]

(11c)[26]: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.41 (d, J = 7.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.15 (dd, J = 7.5, 1.5 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 6.95 (d, J = 8.5 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H).

(1)[11]: ^{1}H NMR (300 MHz, $CDCl_3$, ppm). δ = 10.15 (s, 2H), 8.61 (s, 2H), 8.15 (d, J = 8.1 Hz, 2H), 8.05 (d, J = 7.2 Hz, 4H), 7.74 (d, J = 7.8 Hz, 4H), 7.64 (d, J = 7.8 Hz, 2H, Ar-H), 4.18 (t, J = 7.05 Hz, 4H), 1.72 (br, 4H), 1.25 (br, 36H), 0.87 (t, J = 5.7 Hz, 6H).

(12)[20]: ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.61 (s, 2H, ArH), 8.10 (d, *J* = 5.1 Hz, 2H, ArH), 7.99 (d, *J* = 12 Hz, 2H, ArH), 7.38 (d, *J* = 9.3Hz, 4H, ArH), 6.83 (d, *J* = 8.7 Hz, 4H, ArH), 4.18 (t, *J* = 6.75 Hz, 4 H) 4.00 (s, 4H,), 1.72 (br, 4H), 1.25 (br, 36H), 0.87 (t, J = 5.7 Hz, 6H).

(13)[21]: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.25-7.27 (m, 4H); 7.21-7.24 (m, 4H), 7.05 (d, J = 8.0 Hz, 4H), 6.81-6.85 (m, 16H), 6.73 (d, J = 8.0 Hz, 4H), 6.66 (d, J = 8.0 Hz, 4H), 3.65 (br, 4H).

(15a)[7]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.36 (s, 1H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 5.00 (br s, 1H), 3.59 (t, *J* = 4.95 Hz, 2H), 3.04 (t, J = 4.95 Hz, 2H), 2.42 (s, 3H).

(15b)[7]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.30 (d, *J* = 6.6 Hz, 2H), 4.98 (br s, 1H), 3.64 (t, *J* = 5.1 Hz, 2H), 3.04 (t, J = 5.4 Hz, 2H), 2.41 (s, 3H).

(15c)[7]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 6.3 Hz, 2H), 6.68 (d, *J* = 9 Hz, 2H), 4.78 (br s,1H), 3.60 (s, 2H), 3.02 (br t, 2H), 2.81 (t, J = 7.2, 2H), 2.41 (s, 3H).

(15d)[29]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.63-7.70 (m, 5H), 7.35 (d, *J* = 6.0 Hz, 2H), 5.00 (br s, 1H), 3.23 (t, *J* = 7.7 Hz, 2H), 2.83 (t, J = 6.0 Hz, 2H), 2.38 (s, 3H).

(2): ^{1}H NMR (300 MHz, $CDCl_3$, ppm). δ = 8.56 (s, 2H), 8.20 (d, J = 7.2 Hz, 2H), 7.97 (d, J = 7.8 Hz, 4H), 7.84 (d, J = 7.8 Hz, 4H), 7.70 (d, J = 7.2 Hz, 2H, Ar-H), 4.18 (t, J = 7.05 Hz, 4H), 1.72 (br, 4H), 1.28 (br, 36H), 0.87 (t, J = 6 Hz, 6H). TOF MS ES+: $[M+H]^+$ 967.0084.

Acknowledgements

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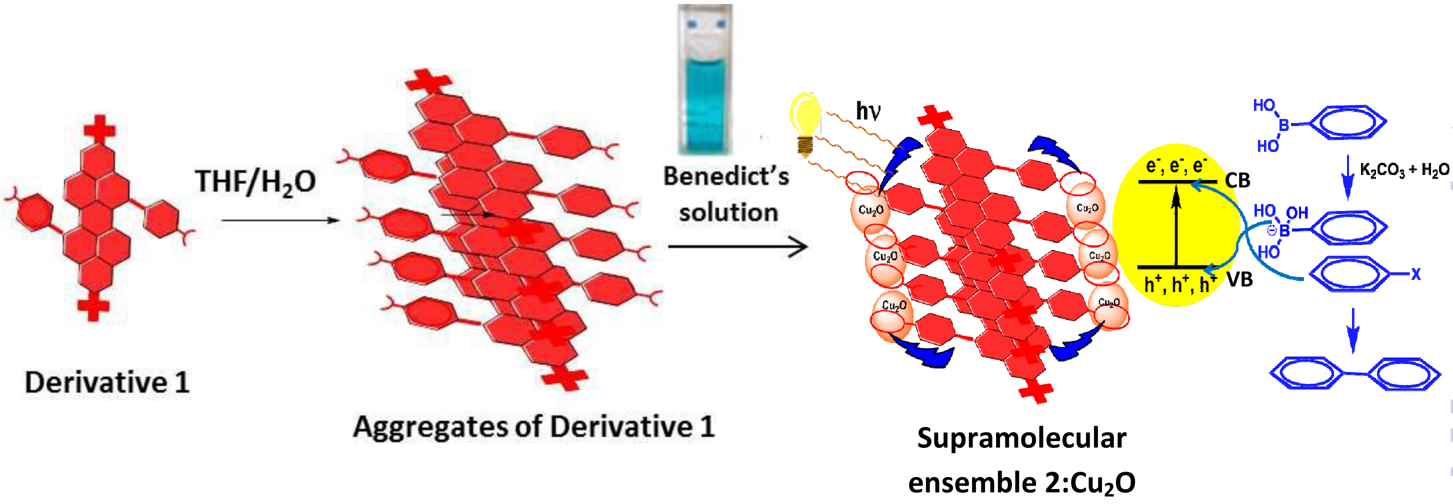

Synopsis

Aggregates of PBI derivative **1** in combination with Benedict's reagent have been as reactors for facile preparation of supramolecular ensemble **2**:Cu$_2$O at room temperature. Interestingly, the *in situ* generated supramolecular ensemble (**2**:Cu$_2$O) of Cu$_2$O NPs and aggregates of oxidized species **2** exhibited excellent photocatalytic efficiency in Suzuki-Miyaura and Suzuki type cross-coupling reactions under mild and eco-friendly conditions.

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