Electronic Supplementary Information

Visible light promoted PANI@Au:CuO catalyzed sequential amination, azidation and annulation for the preparation of 2-arylbenzimidazoles
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**General experimental methods**

“UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer using a quartz cuvette (path length, 1 cm). The fluorescence spectra were obtained with a SHIMADZU 5301 PC spectrofluorimeter. TEM images were recorded in Transmission Electron Microscope (TEM-JEOL 2100F). X-ray diffraction patterns were collected using Rigaku Xpert Pro-X-ray diffractometer provided with CuKα radiation (1.541 Å) in the 2θ range of 5-80⁰C at a step size of 0.02⁰C. The dynamic light scattering (DLS) data were recorded with MALVERN Instruments (Nano-ZS). Infrared spectra were obtained on Varian 660-IR spectrometer using KBr pellets. X-ray photoelectron spectra (XPS) were acquired in PHI Versa Prob 5000. The amount of Au and Cu in catalyst was determined by atomic absorption spectrophotometer (GBC Avant Ver 1.31). Sample preparation was done by reflux assisted digestion of 2 mg of catalyst with concentrated HNO₃. The resulting solution was cooled, centrifuged and filtered. The filtrate was diluted to 10 times with deionized water. Cyclic Voltammetry studies were performed on CH Instruments CH1660D in presence of supporting electrolyte 0.1 M tetrabutylammonium perchlorate (Bu₄NClO₄), Ag/AgCl as reference electrode, platinum wire as counter electrode and glass carbon electrode as working electrode. TEM and HR-TEM images were recorded using HR-TEM-JEM 2100 microscope. To record FT-IR spectra, VARIAN 660 IR Spectrometer was used. Thermogravimetric analysis (TGA) was carried out on EXSTAR TG/DTA 3600 at a heating rate of 100°C/min under nitrogen atmosphere. Photocatalytic experiments were carried out by using the 100 W tungsten filament bulb as irradiation source. ¹H NMR spectra were recorded on a JEOL-FT NMR-AL 400 MHz and Bruker (Avance II) FT-NMR 500 MHz spectrophotometer using DMSO-d₆/CDCl₃ as solvents and tetramethylsilane (Si(CH₃)₄) for internal standards. Further, NMR data was expressed as follows:
chemical shifts in ppm (δ) and coupling constants in Hz (J). Multiplicites of signals were quoted as follows: s = singlet, d = doublet, br s = broad singlet, t = triplet and m = multiplet.”

**Quantum yield calculations**

“To find out the fluorescence quantum yield of derivative 4, solution of diphenylanthracene (Φ_tr = 0.90 in cyclohexane) was used as reference at an excitation wavelength (λ_ex) of 310 nm. Further, the following equation was used to determine the quantum yield:

\[
\Phi_{fs} = \Phi_{fr} \times \frac{1 - 10^{-A_{tr}\Lambda_{tr}}}{1 - 10^{-A_{sr}\Lambda_{sr}}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}
\]

Φ_{fs} and Φ_{fr} signify the fluorescence quantum yields of sample and reference, respectively. L_s, A_s, D_s and N_s are the length of the absorption cells, absorbance, respective areas of emission and refractive index of sample, respectively. L_r, A_r, D_r and N_r are the length of the absorption cells, absorbance, respective areas of emission and refractive index of reference, respectively.”

**EXPERIMENTAL SECTION**

![Scheme S1](image)

Scheme S1 Synthesis of derivative 4

To a mixture of compounds 2 (0.5 g, 1.07 mmol) and 3 (0.52 g, 2.36 mmol) in 20 mL of 1,4-dioxane was added 1 mL of aqueous solution of K_2CO_3 (1.1 g, 8.58 mmol) followed by addition of [Pd(Cl)_2(PPh_3)_2] (0.451 g, 0.64 mmol) under N_2 atmosphere (Scheme S1). The reaction mixture was refluxed for 24 h. After completion of the reaction, the excess solvent was removed under reduced pressure and the residue so obtained was dissolved in DCM. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and removed under reduced pressure to give a crude product which was purified by column chromatography using chloroform/methanol (95:5) as an eluent to afford derivative 4 as orange solid (0.294 g in 56% yield); mp: >280 °C. ^1H NMR
(400 MHz, CDCl₃, ppm) δ = 8.94 (s, 2H), 8.93 (s, 2H), 8.23 (s, 2H), 8.14 (d, J = 8.8 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H); m/z = 529.7838 [M + K]+; IR (KBr): νmax (in cm⁻¹) = 3356 (N-H stretching, asymmetric), 3205 (N-H stretching, symmetric), 1671(s), 1602(s), 1522(s), 1261 (C-N stretching) and 754 (NH₂ wagging). The ¹³C NMR spectrum of derivative 4 could not be recorded due to its poor solubility.

Generation of PANI-5@Au:CuO NCS:

(a) PANI-5@Au:CuO (1:1) NCS

Solutions of 54 μL of Au³⁺ (0.1 M) and 180 μL of Cu²⁺ (0.1 M) ions were simultaneously added to 12 mL of aggregates of derivative 4 (10⁻⁴ M) in H₂O-THF (6:4) solvent mixture with vigorous stirring. During stirring, the color of solution changed from light yellow to green and finally dark brown indicating the generation of PANI-5@Au:CuO NCS. Brown colored precipitates were observed after stirring the reaction mixture continuously for 1h at room temperature. The resulting reaction mixture was sonicated to obtain homogeneous solution.

(b) PANI-5@Au:CuO (1:2) NCS

Solutions of 54 μL of Au³⁺ (0.1 M) and 360 μL of Cu²⁺ (0.1 M) ions were simultaneously added to 15 mL of aggregates of derivative 4 (10⁻⁴ M) in H₂O-THF (6:4) solvent mixture with vigorous stirring for 1h at room temperature. 4.0 mL of this solution was used as such for carrying out sequential amination/azidation/annulation reactions.

(c) PANI-5@Au:CuO (2:1) NCS

Solutions of 108 μL of Au³⁺ (0.1 M) and 180 μL of Cu²⁺ (0.1 M) ions were simultaneously added to 15 mL of aggregates of derivative 4 (10⁻⁴ M) in H₂O-THF (6:4) solvent mixture with vigorous
stirring. 4.0 mL of this solution was used as such for carrying out sequential amination/azidation/annulation reactions.

**General Procedure for Synthesis of Benzimidazole derivatives (8a-8k/8m/8n) using PANI-5 @ Au:CuO nanocomposites.**

In a 50 mL round-bottom flask (RBF), aniline 7a (0.1 g, 1.0 mmol), TMSN$_3$ (2.0 mmol) and methyl benzene 6a (10 mmol) were mixed in DMSO (10 mL) in the presence of PANI-5@Au:CuO NCS (0.01 mmol). The reaction mixture was degassed under vacuum for 2-3 min and then irradiated with a 100 W tungsten filament bulb (0.24 W/cm$^2$) from a distance of 10 cm to provide visible light for 12 h. The reaction temperature was maintained at room temperature by putting RBF in a water bath. After completion of the reaction, the reaction mixture was stirred with saturated Na$_2$SO$_3$ (1 mL) for 1 h and extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and distilled off to yield a residue that was purified by column chromatography using hexane and ethyl acetate as an eluent to afford desired products. The aqueous layer containing nanocomposites was then used as such for further catalytic reactions.
Table S1. Comparison of wet chemical method in present manuscript over other reported procedure in the literature for the preparation of Au-CuO nanocomposites.

<table>
<thead>
<tr>
<th>Journal</th>
<th>Nano composites</th>
<th>Preparation method</th>
<th>Chemicals used</th>
<th>External Reducing/oxidising agent/Surfactant/Base</th>
<th>Temp (°C)</th>
<th>Time</th>
<th>Application</th>
<th>Shape</th>
<th>Size</th>
<th>Recyclability of catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present Manuscript</td>
<td>PANI-5@Au-CuO nanocomposites</td>
<td>Wet Chemical Method</td>
<td>Pentacenequinone derivative 4, Gold Chloride, CuCl₂.2H₂O</td>
<td>No</td>
<td>Room temperature</td>
<td>70 min.</td>
<td>Construction of 2-arylbenzimidazole via sequential amination/azidation/annulation strategy</td>
<td>Irregular</td>
<td>20 nm</td>
<td>Three Times</td>
</tr>
<tr>
<td>J. Am. Chem. Soc., 2017, 139, 8846</td>
<td>Au/CuO</td>
<td>Thermal decomposition method</td>
<td>Cu(acac)₂, tetralin, TBAB, Oleylamine HAuCl₄.3H₂O</td>
<td>Yes</td>
<td>250°C</td>
<td>3 h</td>
<td>CO oxidation reaction</td>
<td>Spherical</td>
<td>8.2-8.4 nm</td>
<td>Two times</td>
</tr>
<tr>
<td>Nanoscale, 2017, 9, 15033</td>
<td>Au-CuO nanoparticles</td>
<td>Co-reduction method</td>
<td>Dry Al₂O₃, NaBH₄, H₂AuCl₄.3H₂O, PVA, urea, Cu(NO₃)₂.3H₂O</td>
<td>Yes</td>
<td>300°C</td>
<td>3 h</td>
<td>CO oxidation reaction</td>
<td>Spherical</td>
<td>5.4 nm</td>
<td>-</td>
</tr>
<tr>
<td>RSC Adv., 2016, 6, 81607</td>
<td>Au-CuO nanohybrids</td>
<td>Wet Chemical Method</td>
<td>N₂H₃H₂O, NaBH₄, Cu(NO₃)₂, PVP, (NH₃.H₂O), NaOH, H₂AuCl₄.4H₂O, L-ascorbic acid, Trisodium citrate</td>
<td>Yes</td>
<td>80°C</td>
<td>4.5 h</td>
<td>Degradation of Rhodamine B</td>
<td>Nanoflakes</td>
<td>100 nm</td>
<td>Five times</td>
</tr>
<tr>
<td>Sci. Rep. 2015, 5,16115</td>
<td>Au/CuO</td>
<td>Electrochemical method</td>
<td>Copper foil, H₂AuCl₄, 3 M NaOH</td>
<td>Yes</td>
<td>180°C</td>
<td>2 h</td>
<td>Glucose detection</td>
<td>Cauliflower</td>
<td>500 nm</td>
<td>-</td>
</tr>
<tr>
<td>RSC Adv., 2015, 5, 9130</td>
<td>Au/CuO</td>
<td>Thermal reduction method</td>
<td>Cu(NO₃)₂.5H₂O, glucose, NaOH, K₃[Fe(CN)₆]₃, uric acid, Aminoethanol, NaAuCl₄.4H₂O, Ascorbic Acid, Sodium citrate</td>
<td>Yes</td>
<td>200°C</td>
<td>2-4 h</td>
<td>Glucose sensor and CO oxidation</td>
<td>Nanosheets</td>
<td>140-200 nm</td>
<td>-</td>
</tr>
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</table>
Table S2. Comparison of catalytic activity of PANI-5@Au:CuO NCS with other transition metal based catalytic systems reported in literature for synthesis of 2-substituted benzimidazoles.

<table>
<thead>
<tr>
<th>Journal Name</th>
<th>Catalyst</th>
<th>Catalyst loading</th>
<th>Ligand/base/Oxidant/ Pressure of gas</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Time</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present Manuscript</td>
<td>PANI-5@Au:CuO NCS</td>
<td>0.01 mmol</td>
<td>-</td>
<td>DMSO</td>
<td>Visible light</td>
<td>10-18 h</td>
<td>61-87%</td>
</tr>
<tr>
<td>Chem. Commun., 2019, 55, 5958-5961</td>
<td>NiCl₂</td>
<td>2.5 mol%</td>
<td>1,10-Phenanthroline, t-BuOK</td>
<td>Toluene</td>
<td>140°C</td>
<td>24 h</td>
<td>30-52%</td>
</tr>
<tr>
<td>J. Org. Chem. 2018, 83, 9553</td>
<td>tridentate ligand based manganese (I) complex</td>
<td>0.05 mmol</td>
<td>t-BuOK</td>
<td>neat</td>
<td>140°C under argon atmosphere</td>
<td>20 h</td>
<td>50-91%</td>
</tr>
<tr>
<td>ChemCatChem, 2018, 10, 1607</td>
<td>Ru (II)-N,N,N,N'-pentacarboxylphenyl-1,2-benzenediimine complex</td>
<td>0.25 mol%</td>
<td>NaBPh₄, dppe</td>
<td>neat</td>
<td>165°C</td>
<td>24 h</td>
<td>18-96%</td>
</tr>
<tr>
<td>Sci. Rep., 2017, 7, 43758</td>
<td>Cu</td>
<td>10 mol%</td>
<td>Ph₃P, K₂CO₃</td>
<td>DMF</td>
<td>135°C</td>
<td>24 h</td>
<td>75-85%</td>
</tr>
<tr>
<td>ACS Catal., 2017, 7, 7456</td>
<td>Co-PNNH complex</td>
<td>5 mol%</td>
<td>NaHBEt₃, t-BuOK, 4A° MS</td>
<td>Toluene</td>
<td>150°C</td>
<td>24 h</td>
<td>28-99%</td>
</tr>
<tr>
<td>Org. Lett., 2017, 19, 6554</td>
<td>Cu(OAc)₂</td>
<td>20 mol%</td>
<td>TBHP</td>
<td>DMSO</td>
<td>80°C</td>
<td>12-25 h</td>
<td>43-77%</td>
</tr>
<tr>
<td>Org. Lett., 2017, 19, 3243</td>
<td>[Cp*IrCl₂]₂</td>
<td>4 mol%</td>
<td>AgNTf₂, Phenylacetic acid</td>
<td>DCE</td>
<td>80°C</td>
<td>12 h</td>
<td>30-99%</td>
</tr>
<tr>
<td>Org. Lett. 2017, 19, 3243</td>
<td>[Cp*IrCl₂]/AgNTf₂</td>
<td>2.5/10 mol%</td>
<td>PiVOH</td>
<td>DCE</td>
<td>100°C</td>
<td>24 h</td>
<td>40-87%</td>
</tr>
<tr>
<td>J. Org. Chem. 2017, 82, 9243</td>
<td>[Rh(COD)Cl]₂</td>
<td>5 mol%</td>
<td>dAr⁷pe, K₂PO₄</td>
<td>Toluene</td>
<td>120°C</td>
<td>24 h</td>
<td>5-97%</td>
</tr>
<tr>
<td>Org. Chem. Front., 2017, 4, 392</td>
<td>Pd(OAc)₂</td>
<td>0.1 mmol</td>
<td>FeCO₃</td>
<td>Ethanol</td>
<td>Microwave irradiation, 100°C</td>
<td>20 min</td>
<td>65-88%</td>
</tr>
<tr>
<td>Dalton Trans., 2017, 46, 15012</td>
<td>RuHCl(CO)(PN-Si(O) complex</td>
<td>0.2 mol%</td>
<td>NaBPh₄</td>
<td>neat</td>
<td>165°C</td>
<td>12 h</td>
<td>64-85%</td>
</tr>
<tr>
<td>Angew. Chem. Int. Ed., 2016, 55, 15175</td>
<td>Co-SiCN nanocomposite</td>
<td>5.0 mol%</td>
<td>5.0 MPa hydrogen pressure</td>
<td>Triethylamine</td>
<td>110°C</td>
<td>24 h</td>
<td>68-91%</td>
</tr>
<tr>
<td>Catal. Sci. Technol., 2016, 6, 1677</td>
<td>Ir/TiO₂-500</td>
<td>0.010 mmol</td>
<td>-</td>
<td>Mesitylene</td>
<td>120°C under argon atmosphere</td>
<td>18 h</td>
<td>54-99%</td>
</tr>
<tr>
<td>J. Org. Chem., 2015, 80, 6102</td>
<td>CuCl₂·H₂O</td>
<td>0.2 equiv.</td>
<td>Bipy, K₂CO₃, O₂ (1 atm)</td>
<td>Toluene</td>
<td>100°C</td>
<td>24 h</td>
<td>27-81%</td>
</tr>
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</table>
Figure S1 UV-vis spectrum of compound 4 in pure THF.

Figure S2 UV-vis spectra showing the variation in absorbance of compound 4 (10 μM) in H₂O-THF mixture with different fractions of H₂O.
Figure S3 UV-vis absorption spectra of compound 4 in H$_2$O-THF (6:4) solvent mixture upon increasing temperature from 25 to 75°C.

Figure S4 Fluorescence spectra of compound 4 (10 μM) in H$_2$O-THF mixture with different water fractions; $\lambda_{ex} = 310$ nm
**Figure S5** TEM image of compound 4 in H$_2$O-THF (6:4) solvent mixture showing formation of aggregates having irregular shape; scale bar 100 nm.

**Figure S6** DLS studies of compound 4 in H$_2$O-THF (6:4) mixture which showed the presence of irregular shaped particles.
The first order rate constant for the formation of gold nanoparticles was calculated from the change in intensity of absorbance of assemblies of derivative 4 at 538 nm wavelength in the presence of Au$^{3+}$ ions at different time interval. From the time vs. absorbance plot at fixed wavelength 570 nm by using first order rate equation, we get the rate constant $k = \text{slope} \times 2.303 = 1.20 \times 10^{-4}$ sec.

**Figure S7** UV-vis spectra of compound 4 (10 μM) upon addition of Au$^{3+}$ ions (18 equiv.) with time in H$_2$O-THF (6:4) solvent mixture showing surface plasmon resonance (SPR) band at 538 nm. Inset showing change in color of solution of aggregates of compound 4 from yellow to blackish-brown with addition of Au$^{3+}$ ions.

**Figure S8** Graphical representation of rate of formation of AuNPs (A) Time (min.) vs. absorbance plot at 538 nm (B) regression plot of A.

<table>
<thead>
<tr>
<th>Regression Statistics</th>
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<tbody>
<tr>
<td>Multiple R</td>
</tr>
<tr>
<td>R Square</td>
</tr>
<tr>
<td>Intercept</td>
</tr>
<tr>
<td>Slope</td>
</tr>
</tbody>
</table>
Figure S9 UV-vis spectra of compound 4 (10 μM) upon addition of Cu\textsuperscript{2+} ions (60 equiv.) with time in H\textsubscript{2}O-THF (6:4) solvent mixture showing surface plasmon resonance (SPR) band at 290 nm. Inset showing change in color of solution of aggregates of compound 4 from yellow to blue and finally to black with addition of Cu\textsuperscript{2+} ions.

<table>
<thead>
<tr>
<th>Regression Statistics</th>
<th></th>
</tr>
</thead>
<tbody>
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<td>Multiple R</td>
<td>0.997032</td>
</tr>
<tr>
<td>R Square</td>
<td>0.994073</td>
</tr>
<tr>
<td>Intercept</td>
<td>0.1551</td>
</tr>
<tr>
<td>Slope</td>
<td>0.01043</td>
</tr>
</tbody>
</table>

Figure S10 Graphical representation of rate of formation of CuO NPs (A) Time (min.) vs. absorbance plot at 290 nm (B) regression plot of A.

The first order\textsuperscript{3} rate constant for the formation of CuO NPs was calculated from the change in intensity of absorbance of assemblies of compound 4 at 290 nm wavelength in the presence of Cu\textsuperscript{2+} ions at different time interval.\textsuperscript{3} From the time vs. absorbance plot at fixed wavelength 290 nm by using first order rate equation, we get the rate constant = k = slope \times 2.303 = 4.0 \times 10^{-4} \text{sec}^{-1}.
Figure S11 Absorption spectra of compound 4 (10 μM) upon addition of 60 equivalents of various metal ions (Au$^{3+}$, Cu$^{2+}$, Fe$^{3+}$, Co$^{2+}$, Cd$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, Hg$^{2+}$, Fe$^{2+}$, Na$^{+}$, K$^{+}$, Zn$^{2+}$, Al$^{3+}$ and Ca$^{2+}$) as their chloride salts in H$_2$O-THF (6:4), buffered with HEPES, pH = 7.0.

Figure S12 Absorption spectra of compound 4 (10 μM) upon additions of 60 equivalents of various metal ions (Ag$^{+}$, Hg$^{2+}$, Co$^{2+}$, Fe$^{2+}$, Li$^{+}$, Mg$^{2+}$, Cd$^{2+}$, Ni$^{2+}$, Pb$^{2+}$, Na$^{+}$, K$^{+}$, Zn$^{2+}$ and Al$^{3+}$) as their perchlorate/nitrate salts in H$_2$O-THF (6:4), buffered with HEPES, pH = 7.0.
Figure S13 UV-vis spectra of aqueous solution of Au-CuO NCS (red line), Au NPs (green line), CuO NPs (pink line) stabilized by assemblies of compound 4.

Figure S14 UV-vis spectra with time for simultaneous addition of aqueous solution of Au$^{3+}$ and Cu$^{2+}$ ions to the assemblies of compound 4.
The first order rate constant for the formation of Au-CuO nanocomposites was calculated from the changes in intensity of absorbance of assemblies of compound 4 at 570 nm wavelength in the presence of Au$^{3+}$ and Cu$^{2+}$ ions at different time interval. From the time vs. absorbance plot at fixed wavelength 570 nm by using first order rate equation, we get the rate constant $k = \text{slope} \times 2.303 = 5.57 \times 10^{-5}$ sec$^{-1}$. 

**Figure S15** Graphical representation of rate of formation of Au-CuO NCS (A) Time (min.) vs. absorbance plot at 570 nm (B) regression plot of A.
Figure S16 SAED pattern of PANI-5@Au:CuO NCS

Figure S17 DLS studies of polymer supported bimetallic Au-CuO NCS indicated the presence of two sets of particles having size of about 43 nm and 220 nm.
Figure S18 X-Ray diffraction pattern of *in situ* generated Au-CuO NCS.

Figure S19 XPS analysis of PANI-5@Au:CuO NCS indicated the presence of Au$^0$ and CuO species along with polyaniline.
Figure S20 TGA of compound 4 and PANI-5@Au:CuO NCS

Figure S21 Cyclic voltammogram of the compound 4 and PANI-5@Au:CuO NCS in H\textsubscript{2}O:CH\textsubscript{3}CN (6:4) containing 0.1 M Bu\textsubscript{4}NClO\textsubscript{4} (supporting electrolyte) and Ag/AgCl (reference electrode).
Table S3. Table showing oxidation and reduction potentials of compound 4 and PANI-5@Au:CuO NCS

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reduction potential (eV)</th>
<th>Oxidation potential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 4</td>
<td>-0.91</td>
<td>0.35</td>
</tr>
<tr>
<td>PANI-5@Au:CuO NCS</td>
<td>-0.46</td>
<td>0.513</td>
</tr>
</tbody>
</table>

Figure S22 FT-IR spectra of compound 4 and PANI-5@Au:CuO NCS
Figure S23 ESI-MS spectrum of trimer formed after oxidation of compound 4 showed a parent ion peak correspond to $[M_t + K]^+$, m/z = 1505.7094.

Figure S24 X-Ray diffraction pattern of polyaniline nanofibres 5.
Figure S25 (A) Fluorescence spectra of oxidized species 5 in H₂O-THF (6:4) solvent mixture upon addition of bare Au-CuO nanocomposites (5 mol%); (B) Spectral overlap of absorption spectrum of Au-CuO NCS and fluorescence spectrum of oxidized species 5 in H₂O-THF (6:4) mixture showing energy transfer from oxidized species 5 to Au-CuO NCS.

Table S4. Selectivity for sequential amination, azidation and annulation reaction between toluene (6a) and aniline (7a) in the presence of TMSN₃ utilizing PANI-5@Au:CuO nanocomposites (1:1) as photocatalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amount (in mmol)</th>
<th>Selectivitya (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzimidazole (8a)</td>
<td>Benzaldehyde (8’a)</td>
</tr>
<tr>
<td>1.</td>
<td>0.768</td>
<td>0.130</td>
</tr>
</tbody>
</table>

aSelectivity (%) = Amount of benzimidazole formed (mmol)/ΣAmount of each product (mmol) X 100
Table S5. Screening data for sequential amination/azidation/annelulation reaction between toluene (6a) and aniline (7a) in the presence of TMSN₃ utilizing various commercially available photocatalysts.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Photocatalyst</th>
<th>Catalyst loading</th>
<th>Yield</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>PANI@Au:CuO NCS (This Work)</td>
<td>0.01 mmol</td>
<td>72%</td>
<td>12 h</td>
</tr>
<tr>
<td>2.</td>
<td>Rhodamine 6G</td>
<td>5 mol%</td>
<td>-</td>
<td>24 h</td>
</tr>
<tr>
<td>3.</td>
<td>Rhodamine B</td>
<td>5 mol%</td>
<td>-</td>
<td>24 h</td>
</tr>
<tr>
<td>4.</td>
<td>9-Fluorenone</td>
<td>5 mol%</td>
<td>-</td>
<td>24 h</td>
</tr>
<tr>
<td>5.</td>
<td>Methylene blue</td>
<td>5 mol%</td>
<td>-</td>
<td>24 h</td>
</tr>
<tr>
<td>6.</td>
<td>Fluorescein</td>
<td>5 mol%</td>
<td>-</td>
<td>24 h</td>
</tr>
<tr>
<td>7.</td>
<td>Alizarin</td>
<td>5 mol%</td>
<td>-</td>
<td>24 h</td>
</tr>
</tbody>
</table>

Table S6 Photocatalytic efficiency of PANI-5@Au:CuO prepared by mixing aggregates of derivative 4, Au³⁺ and Cu²⁺ ions in ratio of 2:1:1 for carrying out sequential amination, azidation and annelulation reactions between toluene (6a) and aniline (7a) in presence of TMSN₃.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>PANI-5@Au:CuO NCS</th>
<th>Catalytic Cycle</th>
<th>Time (in h)</th>
<th>Yield of 8a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Prepared by mixing aggregates of derivative 4, Au³⁺ and Cu²⁺ ions in ratio of 2:1:1</td>
<td>1st</td>
<td>14 h</td>
<td>70%</td>
</tr>
<tr>
<td>2.</td>
<td>Prepared by mixing aggregates of derivative 4, Au³⁺ and Cu²⁺ ions in ratio of 2:1:1</td>
<td>5th</td>
<td>14 h</td>
<td>65%</td>
</tr>
<tr>
<td>3.</td>
<td>Prepared by mixing aggregates of derivative 4, Au³⁺ and Cu²⁺ ions in ratio of 2:1:1</td>
<td>6th</td>
<td>14 h</td>
<td>63%</td>
</tr>
<tr>
<td>4.</td>
<td>Prepared by mixing aggregates of derivative 4, Au³⁺ and Cu²⁺ ions in ratio of 2:1:1</td>
<td>7th</td>
<td>14 h</td>
<td>58%</td>
</tr>
</tbody>
</table>
Table S7. Effect of addition of TEMPO on sequential amination/azidation/annulation reaction utilizing PANI-5@Au:CuO NCS as photocatalyst

![Chemical reaction](image)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>TEMPO</th>
<th>Yield of 8a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.0 equiv.</td>
<td>72%</td>
</tr>
<tr>
<td>2.</td>
<td>1.0 equiv.</td>
<td>40%</td>
</tr>
<tr>
<td>3.</td>
<td>2.0 equiv.</td>
<td>12%</td>
</tr>
</tbody>
</table>

**Figure S26** IR spectra of intermediate E.
Figure S27 (a) Reaction mixture of aniline (1.0 mmol), toluene (10 mmol), TMSN₃ (2.0 mmol) and PANI-5@Au:CuO NCS (0.01mmol) as catalyst after irradiation of 8 h; (b) After addition of mixture containing KI (1.0 × 10⁻¹ M) and aqueous acetic acid (1.0× 10⁻¹ M), color of solution changes to brown.

Figure S28 Iodometric test for detection of H₂O₂. (A) Reaction mixture; (B) Decolorization of reaction mixture on treatment with 3.5 M H₂SO₄; (C) Addition of 1% KI and 2 drops of ammonium molybdate changed the color of solution to yellow; (D) Addition of freshly prepared starch solution changed the color of solution to blue.
Figure S29 Detection of formation of H$_2$O$_2$ by monitoring the absorption spectra of I$_3^-$ in aqueous media.

![Graph showing absorption spectra with peaks at 298 nm and 367 nm.]

Wavelength (nm) | Absorbance
--- | ---
260 | 0
298 | 0.4
367 | 0.8
500 | 0
620 | 0

figure: $\text{I}^- + \text{H}_2\text{O}_2 \rightarrow \text{I}_2 + \text{I}^- \rightarrow \text{I}_3^-$

Figure S30 (A) Picture of the uncoated paper strip; (B) SEM image of uncoated paper strip; (C) Picture of dip coated paper strip with PANI-5@Au:CuO NCS; (D) SEM image of coated paper strip with PANI-5@Au:CuO NCS.
Figure S31 SEM image of recycled dip coated paper strip after three cycles.
**Compound 8’a** Colorless liquid; Benzaldehyde: (0.014 g in 12% yield). $^1$H NMR (400 MHz, CDCl$_3$, ppm) δ=10.03 (s, 1H), 7.90 (d, $J = 7.2$ Hz, 2H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.55 (t, $J = 7.4$ Hz, 2H).

**Figure S32** $^1$H NMR spectrum of compound 8’a
6a-Tempo adduct: Colorless oil; 1-(Benzyloxy)-2,2,6,6-tetramethylpiperidine: (0.106 g in 40% yield). $^1$H NMR (300 MHz, CDCl$_3$, ppm) $\delta$ 7.36-7.27 (m, 5H), 4.84 (s, 2H), 1.60-1.48 (m, 6H), 1.26 (s, 6H), 1.16 (s, 6H)

Figure S33 $^1$H NMR spectrum of 6a-TEMPO adduct
**Compound 8a** White solid; 2-Phenylbenzimidazole: (0.149 g in 72% yield). $^1$H NMR (500 MHz, DMSO-d$_6$, ppm): 12.90 (br s, 1H), 8.17 (d, $J$ = 8.0 Hz, 2H), 7.66-7.48 (m, 5H), 7.21-7.20 (m, 2H).

**Figure S34** $^1$H NMR spectrum of compound 8a
Compound 8b
White solid; 2-(p-Tolyl)-1H-benzo[d]imidazole: (0.179 g in 80% yield). $^1$H NMR (500 MHz, DMSO-d$_6$, ppm) δ 12.79 (br s, 1H), 8.06 (d, $J = 8.5$ Hz, 2H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.21-7.16 (m, 2H), 2.38 (s, 3H)

Figure S35 $^1$H NMR spectrum of compound 8b
**Compound 8c** White solid; 2-(4-Methoxyphenyl)-1H-benzo[d]imidazole: (0.197 g in 82% yield). $^1$H NMR (500 MHz, DMSO-d$_6$, ppm) $\delta$ 12.72 (br s, 1H), 8.11 (d, $J$ = 8.5 Hz, 2H), 7.61 (d, $J$ = 7.0 Hz, 1H), 7.49 (d, $J$ = 7.0 Hz, 1H), 7.18-7.15 (m, 2H), 7.11 (d, $J$ = 8.5 Hz, 2H), 3.84 (s, 3H)

**Figure S36** $^1$H NMR spectrum of compound 8c
Compound 8d\textsuperscript{9,10} White solid; 2-(4-bromophenyl)-1H-benzo[d]imidazole; (0.188 g in 64% yield). $^1$H NMR (500 MHz, DMSO-d\textsubscript{6}, ppm) $\delta$ 12.99 (br s, 1H), 8.11 (d, $J = 8.5$ Hz, 2H), 7.77 (d, $J = 8.5$ Hz, 2H), 7.60 (s, 2H), 7.23-7.21 (m, 2H)

![Figure S37](image)

Figure S37 $^1$H NMR spectrum of compound 8d
**Compound 8e** White solid; 2-(4-chlorophenyl)-1H-benzo[d]imidazole: (0.150 g in 61% yield). $^1$H NMR (500 MHz, DMSO-d$_6$, ppm) δ 12.98 (br s, 1H), 8.18 (d, $J = 8.5$ Hz, 2H), 7.63 (d, $J = 8.5$ Hz, 3H), 7.54 (s, 1H), 7.22 (s, 2H)

![Figure S38 $^1$H NMR spectrum of compound 8e](image-url)
**Compound 8f** Yellow solid; 2-(4-nitrophenyl)-1H-benzo[d]imidazole: (0.157 g in 61% yield). $^1$H NMR (500 MHz, DMSO-d$_6$, ppm) $\delta$ 13.28 (br s, 1H), 8.42 (s, 4H), 7.72 (s, 1H), 7.61 (s, 1H), 7.27 (s, 2H)

*Figure S39* $^1$H NMR spectrum of compound 8f
**Compound 8g** White solid; 2-(m-tolyl)-1H-benzo[d]imidazole: (0.170 g in 76% yield). $^1$H NMR (500 MHz, DMSO-d$_6$, ppm) δ 12.84 (s, 1H), 8.02 (s, 1H), 7.96 (d, $J$ = 7.5 Hz, 1H), 7.65-7.51 (m, 2H), 7.43 (t, $J$ = 7.5 Hz, 1H), 7.31 (d, $J$ = 7.5 Hz, 1H), 7.21-7.18 (m, 2H), 2.42 (s, 3H).

**Figure S40** $^1$H NMR spectrum of compound 8g
**Compound 8h** White solid; 2-(o-toly)-1H-benzo[d]imidazole: (0.165 g in 74% yield). $^1$H NMR (500 MHz, DMSO-d$_6$, ppm) $\delta$ 12.59 (s, 1H), 7.73 (d, $J = 7.5$ Hz, 1H), 7.67 (d, $J = 7.5$ Hz, 1H), 7.52 (d, $J = 7.5$ Hz, 1H), 7.39-7.35 (m, 3H), 7.24-7.17 (m, 2H), 2.60 (s, 3H).

**Figure S41** $^1$H NMR spectrum of compound 8h
**Compound 8i** White solid; 2-(3,5-Dimethylphenyl)-1H-benzo[d]imidazole: (0.200 g in 84% yield). $^1$H NMR (500 MHz, DMSO-d$_6$, ppm) $\delta$ 12.80 (br s, 1H), 7.80 (s, 2H), 7.63 (s, 1H), 7.50 (s, 1H), 7.19 (s, 2H), 7.13 (s, 1H), 2.37 (s, 6H).

**Figure S42** $^1$H NMR spectrum of compound 8i
**Compound 8j** White solid; 6-Bromo-2-(3,5-dimethylphenyl)-1H-benzo[d]imidazole: (0.122 g in 70% yield). $^1$H NMR (500 MHz, DMSO- $d_6$, ppm) δ 13.02 (br s, 1H), 7.79 (s, 2H), 7.66-7.47 (m, 2H), 7.33 (s, 1H), 7.15 (s, 1H), 2.37 (s, 6H)

![Figure S43 $^1$H NMR spectrum of compound 8j](image)
**Compound 8k** White solid; 6-Chloro-2-(3,5-dimethylphenyl)-1H-benzo[d]imidazole: (0.131 g in 65% yield). $^1$H NMR (500 MHz, DMSO-d$_6$, ppm) $\delta$ 13.02 (br s, 1H), 7.79 (s, 2H), 7.68-7.63 (m, 1H), 7.53 (s, 1H), 7.22 (d, $J = 5.5$ Hz, 1H), 7.15 (s, 1H), 2.37 (s, 6H)

![1H NMR spectrum of compound 8k](image)

**Figure S44** $^1$H NMR spectrum of compound 8k
**Compound 8m** White solid; 2-(3,5-Dimethylphenyl)-4-methyl-1H-benzo[d]imidazole: (0.181 g in 82% yield). mixture of tautomers (1:1); $^1$H NMR (500 MHz, DMSO-d$_6$, ppm) δ 12.73 (br s, 1H), 12.48 (br s, 1H), 7.86 (s, 2H), 7.79 (s, 2H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.12-7.07 (m, 4H), 6.99-6.96 (m, 2H), 2.57 (s, 3H), 2.55 (s, 3H), 2.37 (s, 12H)

![Figure S45 $^1$H NMR spectrum of compound 8m](image)
**Compound 8n** White solid; 2-(3,5-Dimethylphenyl)-4,7-dimethyl-1H-benzo[d]imidazole: (0.180 g in 87% yield).

$^1$H NMR (500 MHz, DMSO-d$_6$, ppm) δ 12.40 (br s, 1H), 7.88 (s, 2H), 7.12 (s, 1H), 6.87 (s, 2H), 2.53-2.51 (m, 6H), 2.39 (s, 6H)

*Figure S46 $^1$H NMR spectrum of compound 8n*
**Compound 4** Orange solid; (0.294 g in 56% yield) $^1$H NMR (400 MHz, CDCl$_3$, ppm) $\delta = 8.94$ (s, 2H), 8.93 (s, 2H), 8.23 (s, 2H), 8.14 (d, $J = 8.8$ Hz, 2H), 7.94 (d, $J = 8.8$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 7.61 (d, $J = 8.8$ Hz, 2H), 7.53 (d, $J = 8.8$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H)

![Figure S47 $^1$H NMR spectrum of compound 4](image-url)
Figure S48 Mass spectrum of compound 4.
REFERENCES: