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## Sulphonic Acid Functionalized Porphyrin Anchored with meso-Substituted Triazolium Ionic Liquid Moiety: Heterogeneous Photo-Catalyst for Metal/Base Free C-C Cross-Coupling and C-N/C-H activation using Aryl Chloride under visible light irradiations

Karan Bhansali, Subodh Raut, Shital Barange and Pundlik Bhagat\*

We report an easy process to synthesize sulphonic acid functionalized porphyrin, anchored with meso-substituted triazolium ionic liquid moiety (SAFPTILM) for metal/base free C-C cross-coupling and C-N/C-H activation using aryl chloride under visible light irradiations. The acid strength has been measured by Hammett indicator. The SAFPTILM photocatalyst comprising 18  $\pi$ -conjugated electronic systems, with the chromophore substituents on the meso-position can provide rapid electronic conducting channels during photocatalysis by irradiation of visible light. It was found that the SAFPTILM is an efficient photocatalyst for the Heck, Sonogashira, Buchwald, Ullmann/Fittig coupling and C-H activation of phenols with different aryl chlorides in absence of base/noble metal, using 5 W LED (yellow) light at ambient conditions. The low band gap (1.55 eV) of SAFPTILM with conjugation assists photocatalytic reaction using inactivated aryl chlorides, by easy excitation of electrons and transfer to the conjugated benzimidazlium based phenylene di-imine support delaying the recombination of photoinduced electron-hole pairs.

(ROS),

TiO<sub>2</sub>

species

assisted

solar

/phthalocyanine<sup>4,5</sup> also have attracted tremendous

interests pointing to constantly refine their performance in the production of reactive oxygen

especially

photodynamic cancer therapies, artificial light

harvesting, optoelectronic devices, various sensor

technologies<sup>7</sup> and light energy conversion.<sup>8</sup> Hasobe

et al. have reported that porphyrin-based

nanoarchitectures applicable for light energy

conversion.<sup>9</sup> Moreover, they have revealed CTAB-

pyridyl)porphyrin hexagonal nanocylinders which

afford effective under visible light for the

generation of hydrogen.<sup>10</sup> McHale and his co-

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#### 1. Introduction

Photosynthesis is the only important solar energy harnessing process, promoting animal and plant life on the Earth. It is the source of all of our food and most of the energy resources acquired by absorbing light energy by chlorophyll. Chlorophyll is one of the key biological molecules for all phototrophic organisms which contain tetra-pyrrolic porphyrin units containing magnesium atom at its center.<sup>1</sup> Taking motivation from these, various technologies have been emerged making use of synthetic chlorins or porphyrins to imitate photosynthesis artificially, needing molecules with good absorption in visible range and other photophysical and redox characteristics.<sup>2,3</sup> Besides, with the rapid development of different photocatalytic processes the past few decades, bio-inspired over photosensitizers containing porphyrin

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workers have described that self-assembled structures of porphyrin have prospective role in cell and Additionally, surfactant aided nanospheres and nanorods of zinc meso-tetra(4-pyridyl) porphyrins have also been testified recently, for photocatalytic applications.<sup>12</sup> porphyrinoids and their metal complexes have been widely used in the process of photocatalysis and environmental remediation, playing the key role of tentacles for light-sensing probes. The

oxygen<sup>6</sup>

meso-tetra(4-

devices.<sup>11</sup>

porphyrins,

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spectacular performance perceived due to their slight singlet-triplet splitting, the high quantum yield for the intersystem channel, and the extensive triplet-state life span. Consequently, they are chemical stabilizers magnificent and photosensitizers under visible light irradiation.<sup>13</sup> Porphyrin molecules are identified to form aggregates even in homogeneous solution.<sup>14</sup> Among different aggregates described on porphyrin moieties, two types of aggregates are reflected to be very significant one is the H-aggregates, where hypsochromic shift is observed due to face-to-face arrangement of molecules and the other Jaggregates, in which bathochromic shift is dominated due to side-by-side arrangement of molecules.<sup>15</sup> Mandal et al. have fabricated 1hexadecyl-3-methylimidazolium bromide-assisted zinc octaethylporphyrin (ZnOEP) nanoaggregates and confirm the H-aggregation of porphyrin during the formation. It was confirmed that IL-supported ZnOEP indicated high efficiency in transfer of energy from porphyrin to phthalocyanine compare to analogous protocol in organic solvent.<sup>16</sup> Thus literature study identified the crucial role of IL in porphyrin aggregation and enhancement of energy transfer. Taking inspiration from these, our research group engaged with the design and fabrication of porphyrin and phthalocyanine photosensitizers to imitate artificial photosynthesis for harvesting of visible light with good extinction coefficient.

42 One of the ways of energy sustainability is to make 43 viable utilization of light energy to drive chemical 44 transformations. Our research group has 45 46 successfully reported a polymer-supported salen-47 palladium complex as a heterogeneous catalyst for 48 the Mizoroki-Heck cross-coupling reaction and the 49 Suzuki-Miyaura cross coupling in neat water.<sup>17</sup> 50 Waghmode et al. have developed a reusable 51 52 PdCl<sub>2</sub>/TiO<sub>2</sub> for C-C coupling reaction for different 53 substituted aryl iodides with olefins under UV-54 visible light which affords good yield for the 55 corresponding products at ambient reaction 56 conditions.<sup>18</sup> Further visible light-mediated metal 57 58 free<sup>19</sup> Pd-Ru-catalyzed ligand free Heck reaction 59

was revealed with a great prospective for the broad range synthetic utility with (E)-selectivity of corresponding products from aryl iodides.<sup>20</sup> Javier F. Guastavino and co-workers reported metal free, t-BuOK base catalysed process for the synthesis of E-stilbene by direct C-H arylation of alkenes with a wide range of aryl halides, including ArCl using 400 W lamps.<sup>21</sup> The UV light induced reaction applied for the construction of C-C, C-N bonds using aryl chlorides and inert arenes in absence of catalyst.<sup>22</sup> The metal/base free, mild reaction protocol also afforded the trifluoromethylation products under the optimized conditions tolerating electron donating and withdrawing groups. Louis Onuigbo's group recently described a metal-free Heck coupling technique, efficiently applied to a wideranging substrates including heteroaromatics, with electron-donating substituents strong on diarylethylenes under mild conditions, under simulated or natural sunlight.<sup>23</sup> Recently, a recyclable Pd-rGO/CNT/CaFe<sub>2</sub>O<sub>4</sub> nanocomposite with high multifunctional photocatalytic activity under visible light irradiation established towards the Heck reaction involving aryl iodides to achieve the product in good to excellent yields.<sup>24</sup> Recently, we have synthesized polymer supported Fephthalocyanine knotted with carboxyl functionalized benzimidazolium moiety for efficient visible-light-driven degradation of organic dyes from aqueous solutions. The photocatalyst excellent activity presented towards the degradation of dyes, without any additives such as  $ZnO/TiO_2$  in the presence of 5 W LED lamp as a source of light.<sup>25</sup> More recently, our group reported perylene supported metal free brønsted acidfunctionalized porphyrin intertwined with benzimidazolium moiety for sustainable etherification of furfuryl alcohol with various alcohols under irradiation of yellow visible (5 W LED) light.<sup>26</sup>

Yet, to influence a high and competent conversion of simulated light energy into chemical energy is still a great exciting task. As the reports on the vinylation or arylation of olefins by C-Cl bond activation are restricted, finding a highly dynamic

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and recyclable heterogeneous metal/base free photo-catalyst would be highly desirable. Furthermore special devotion should be paid to the design of photocatalytic materials for metal/base free C-C/C-N coupling in presence of visible light irradiation.<sup>27</sup> To the best of our knowledge, there is no article on porphyrin based photocatalyst which could be convenient for C-C coupling in absence of base or precious metal. Accordingly, our research group committed making use of light energy for organic transformations at ambient conditions. To explore the concept, we describe synthesis of Brønsted acid functionalized porphyrin, tangled with triazolium moiety, offering photocatalytic applications in metal/base free C-C cross-coupling (Heck/Sonogashira), C-H/C-N (Buchwald-Hartwig) activation and Fittig/Ullmann type coupling using unactivated aryl chloride under 5 W light irradiations.

We establish that visible light can stimulate these C-C/C-N coupling and C-H activation reactions with SAFPTILM photocatalyst the at ambient temperature, in home-made photo-reactor and the rate of photocatalysis influence on the intensity and wavelength of the light irradiation. The mechanism of light excited cross coupling reaction and recyclability heterogeneous photocatalyst were also illustrated. It is sensible to assume that the SAFPTILM photocatalyst is prospective for driving a variety of metal/base free cross-coupling and C-N/ C-H activation reactions with visible light. It may be noted that the activation of various aryl chlorides for different reactions may not be the same, but the affording of several cross-coupling reactions can offer perception into the mechanism of the photocatalytic cross-coupling progressions in general.

## 2. Experimental

## 2.1. Materials

p-Phenylenediamine (PPD) was delivered by Avra. Hydrochloric acid (35.8-38.0%), Sodium Sulphate

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(99.5%) and Methanol (99.9%) were purchased from Fisher Scientific. Formaldehyde Solution (37-41% w/v AR), Sodium Hydride (60% dispersion in Paraffin Oil) and Sodium hydroxide, Chloroform-d (99.8 atom % D for NMR Spectroscopy), Pyrrole and Salicylaldehyde were acquired from S D Fine-Chem. Ltd. Acetic acid was received from Sigma Aldrich. Triazole (99% Spectrochem), Dimethyl Sulfoxide-d6 (deuteration degree min. 99.8% for NMR Spectroscopy), Chloroform and Ethyl Acetate (99%) and Tetrahydrofuran were provided by Sisco Research Laboratories Pvt. Ltd. All of these reagents were used as received without any further purification unless otherwise recommended.

#### 2.2. Characterization techniques

<sup>1</sup>H NMR and <sup>13</sup>C spectra of intermediates were analysed with Bruker spectrometer operating at 400 MHz at ambient temperature; using DMSO-d6 and CDCl<sub>3</sub> as solvent; and TMS ( $\delta$  = 0.00) for <sup>1</sup>H calibration. FT-IR spectra were found from IR affinity 1 Shimadzu FT-IR spectrophotometer using KBr pellet method. Surface morphology and the elemental composition of the complex were examined by scanning electron microscope (SEM) along with energy dispersive X-ray (EDAX) spectroscopy (Carl Zeiss EVO/18SH, UK). An accelerating voltage of 10 kV was applied to obtain SEM images. Thermal stability of SAFPTILM was studied using TGA thermoanalyser SII, 7200 (Seiko, Japan). UV-Vis-NIR Spectrophotometer (Jasco ISN-723, Sr. no. B 072061154, Made in Japan) was used to assess DRS-Spectra of solid SAFPTILM photocatalyst. BET (Autosorb IQ Surface Area Gas Sorption Analyzer from Quantachrome, made in Japan) elemental analysis was supported to know pore diameter and total surface of area of photocatalyst.



Scheme 1 Synthesis of 1a

#### 2.3. Synthesis of SAFPTILM

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## 2.3.1 Synthesis of 3-(chloromethyl)-2hydroxybenzaldehyde (1a)

The synthesis of 1a was achieved by adapting procedure from the known literature.<sup>28</sup> In a 50 mL round bottom flask (RBF), the mixture of Conc. HCl (30 mL) and formaldehyde (3 mL, 100 mmol) was cooled at 0 °C and allowed constant stirring for 30 min. To this mixture, salicylaldehyde (2.92 mL, 24 mmol) was charged gradually and reaction mixture was kept on magnetic stirring for 44 - 48 h at room temperature (RT). The precipitated desired 1a solid (white) was separated and washed with 3 x 10 mL distilled water, followed by acetone and recrystallized from n-hexane. The resulting compound (1a) was dried in hot air oven for 12 h and used for next step. (3.5 g, Yield: 87 %)

<sup>1</sup>H NMR (400MHz, DMSO) δ = 10.92 (s, 1H), 10.27 (s, 1H), 7.72 (d, 1H), 7.58 (q, 1H), 7.02 (d, 1H), 4.75 (s, 2H). <sup>13</sup>C NMR (100MHz, DMSO) δ = 191.19, 161.20, 137.43, 129.59, 129.27, 122.44, 118.22, 44.16. FT-IR – 3213.41, 2875.86, 1649.14, 1620.21, 1577.77, 1475.54, 1436.97, 1379.10, 1280.73, 1255.66, 1186.22, 1145.72, 1114.86, 1008.77,

947.05, 902.69, 846.75, 767.67, 717.52, 686.66, 659.66, 572.86, 497.63, 449.41.

## 2.3.2 Synthesis of 3-((2H-1,2,3-triazole-2yl)methyl)-2-hydroxybenzaldehyde (1b)

To a 100 mL RBF sodium hydride was placed and mixed with 30 mL n-hexane. The reaction mixture was stirred at room temperature for 40 min., after which time the excess solvent was decanted under vacuum to remove paraffin oil.<sup>29</sup> The flask containing NaH (1.32 g, 55 mmol) was charged with 15 mL tetrahydrofuran (THF), cooled in ice bath to maintain 2 to 3 °C temperature, and solution of triazole (3.45 g, 50 mmol) in THF was added dropwise and stirred for 2 h at cold condition. The loaded with reaction mixture was chloromethylated salicylaldehyde (1a) (8.50 g, 50 mmol) in THF very slowly at the same temperature. The reaction mixture was then reflux for 44 - 48 h (60 °C). After cooling, the salt was removed by filtration and the solvent was evaporated under vacuum by rotavapour to get sticky yellowish liquid. The product was charged with the mixture of ethyl acetate and saturated brine solution to remove remaining salt. The organic layer was separated and dried using anhydrous sodium sulphate for overnight. The ethyl acetate layer was concentrated using rotavapour to get sticky vellowish solid. The resulting solid was rinsed by diethyl ether (3 X 10 mL) and dried in hot air oven







to afford yellowish fine powder 1b. Yield- 84%, 8.5 gram.

<sup>1</sup>H NMR (400MHz, DMSO) δ = 10.26 (s, 1H), 8.64 (s, 1H), 7.97 (s, 2H), 7.59 (s, 1H), 7.47 (d, 1H), 6.99 (d, 1H), 5.35 (s, 2H). <sup>13</sup>C NMR (100MHz, DMSO) δ = 191.20, 161.44, 152.21, 144.48, 136.61, 128.60, 127.43, 122.68, 118.29, 51.71

## 2.3.3 Synthesis of 2-(3-formyl-2hydroxybenzyl)1,3-bis(4-sulfobutyl)-2H-1,2,3triazole1,3-diium hydrogen sulfate (1c)

1, 4-Butylsultone (6.80 g, 50 mmol) was added slowly to a 30 mL solution of triazole salicylaldehyde (5.08 g, 25 mmol) (1b) in acetonitrile into a flask and the mixture was refluxed with constant stirring for 44 - 48 h. The solvent was evaporated to dryness by rotavapor and the resulting zwitter ion intermediate was quenched with 10% (1ml of H<sub>2</sub>SO<sub>4</sub> in 10 ml of H<sub>2</sub>O) aq. H<sub>2</sub>SO<sub>4</sub> solution.<sup>30</sup> The reaction mixture was refluxed for 12 h, after which time the excess sulfuric acid was evaporated under vacuum. The solid sticky product was washed with diethyl ether (3 x 10 mL), to achieve pure sticky product (1c) confirm by by <sup>1</sup>H NMR and <sup>13</sup>C NMR. Yield=89%, 15 g. <sup>1</sup>H NMR (400MHz, DMSO) δ = 10.21 (s, 1H), 9.42 (s, 1H), 9.19 (s, 1H), 8.63 (s, 4H), 7.68 (s, 1H), 7.55 (d, 1H), 7.02 (d, 1H), 5.47 (s, 2H), 3.36 (t, 4H), 2.05 (t, 2H), 1.72 (t, 2H), 1.62 (t, 4H), 1.45 (t, 4H). <sup>13</sup>C NMR (100MHz, DMSO) δ = 191.32, 161.35, 142.99, 142.87, 137.19, 129.58, 122.64, 118.25, 74.97, 70.10, 60.89, 51.66, 48.27, 31.87, 23.30, 22.90, 22.10, 21.81.

## 2.3.4 Synthesis of phenylene bis (azanylylidene))bis(methanylylidene))bis(2-(chloromethyl)phenol) (2a)

p-Phenylenediamine (2.16 g, 20 mmol) and chloromethylated salicylaldehyde (1a, 6.80 g, 40 mmol) were weighed and mixed into a 100 mL RBF containing 30 mL methanol and the mixture was refluxed with a magnetic stirring for 3 h.<sup>31</sup> The reaction mixture was cooled to RT affording the product as a red colour solid product in quantitative yield. The resulting product was washed with methanol to acquire red colour solid, obtained by filtering and dried in hot air oven at 80 °C. Yield = 92%, 14.5 g.

<sup>1</sup>H NMR (400MHz, DMSO) δ = 8.65 (d, 2H), 8.63 (d, 2H), 8.54 (s, 4H), 8.45 (s, 2H), 8.18 (d, 2H), 6.55 (s, 2H), 5.01 (s, 4H). <sup>13</sup>C NMR (100MHz, DMSO) δ = 166.048, 152.10, 136.61, 133.40, 130.38, 125.37, 118.71, 61.16

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## 2.3.5 Synthesis of 3-((1H-benzo[d]imidazole-1yl)methyl)-2-hydroxybenzaldehyde(2b)

To a 100 mL RBF sodium hydride was placed and 30 mL n-hexane was added and the reaction mixture was stirred at RT for 40 min., after which time the excess solvent was decanted under vacuum to remove paraffin oil. The flask containing NaH (0.96g, 40 mmol) was charged with 15 mL tetrahydrofuran (THF), cooled in ice bath to maintain 2 to 3 °C temperature, and solution of benzimidazole (2.36 g, 20 mmol) in THF was added gradually and stirred for 2 h at cold condition. The reaction mixture was charged with chloromethylated salicylaldehyde (1a) (3.41 g, 20 mmol) in THF steadily at the same temperature. The reaction mixture was then refluxed for 44 - 48 h (60 °C). After cooling, the salt was discarded by filtration and the solvent was concentrated under vacuum by rotavapour to get sticky yellowish liquid. To the product the mixture of ethyl acetate and saturated brine solution was added to remove remaining salt. The organic layer was separated and dried using anhydrous sodium sulphate for 12 h. The ethyl acetate layer was evaporated using rotavapour to get sticky yellowish solid.<sup>32</sup> The resulting solid was washed by diethyl ether (3 X 10 mL) and dried in hot air oven to obtain yellowish fine powder 2b. Yield- 82 %, 8.2 gram.

#### <sup>50</sup> <sup>1</sup>H NMR (400MHz, CdCl<sub>3</sub>-d6) δ 11.03 (s, 1H),

<sup>52</sup> 9.81 (s, 1H), 7.97 (s, 1H), 7.83 (d, 2H), 7.39 (d, 1H),
<sup>53</sup> 7.26-7.27 (m, 3H), 6.99 (d, 1H), 5.20 (s, 2H).

# 2.3.6 Synthesis of 1,1'-((((((1E, 1'E)-1,4-phenylenebis(methanylylidene))bis(methylene))b is(2-hydroxy-3,1-

## phenylene))bis(methylene))bis(3-(3-formyl-2hydroxybenzyl)-1H-benzo[d]imidazole-3-ium) chloride (2c)

In a 50 mL RBF, the mixture of phenylene bis (azanylylidene))bis(methanylylidene))bis(2-

(chloromethyl)phenol) 2a (0.412 g 1 mmol) and benzamidazole salicylaldehyde 2b (0.504 g, 2 mmol) was suspended in 30 mL chloroform. The mixture was set aside on constant stirring for 44 -48 h.<sup>33</sup> After the completion of reaction, the precipitated NaCl salt was separated by filtration and rinsed with chloroform twice. The resulting filtrate was concentrated under vacuum to acquire precipitate, dried in hot air oven to give 2c.Yield: 74 %, 14.2 g.

<sup>1</sup>**H NMR (400MHz, DMSO) δ** = 10.88 (s, 2H), 10.22 (s, 2H), 8.60 (s, 2H), 8.88 (s, 2H), 7.55-7.57 (m, 6H), 7.51 (d, 5H), 0.00-7.01 (m, 4H), 6.99 (s, 5H), 5.46 (s, 4H), 4.64 (s, 4H), 3.92 (s, 2H), 3.36 (s, 4H). **FT-IR.** 3535.52, 3109.25, 3055.24, 1774.51, 1707, 1618.28, 1533.41, 1458.18, 1413.82, 1340.53, 1313.52, 1168.86, 1145.72, 1109.07, 1060.85, 985.62, 937.40, 867.97, 823.60, 765.74, 715.59, 661.94, 623.01, 603.72, 567.07, 516.92, 465.20

2.3.7 Synthesis of 2-(3-((15,20-bis(3-((1,3-bis(4-sulfobutyl)-2H-1,2,3-triazole-1,3diium2yl)methyl)-2-hydroxybenzyl)-10-(2-hydroxy-3-((1-(2-hydroxy-3-((((E)-4-(E)-((2-hydroxy-3-((3-(2hydroxy3((10,15, 20-tris(3-((1,3-bis(4-sulfobutyl)-2H-1,2,3-triazole-1,3-diium-2-yl)methyl)2hydroxybenzyl)porphyrin-5-yl)methyl)benzyl)-1H-benzo[d]imidazole-3-ium-1yl)methyl)benzyl)imino)benzylidene)amino)met

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## hyl)benzyl)1Hbenzo[d]imidazole3ium1yl)methyl) benzyl)imino)methyl)benzylidene)amino)methyl) benzyl)1Hbenzo[d]imidazol3ium3yl)methyl)benzy l)Porphyrin-5-yl)methyl)2hydroxybenzyl)1,3bis(4sulfobutyl)-2H-1,2,3-triazole-1,3-diium dichloride dodecakis (hydrogen sulphate)

HO сı 'nн снсіз Reflux 44 - 48 h OFHC CI CI [1:2] 2c 7 3,3'-((((((1*E*,1'*E*)-1,4-phenylenebis(methanylylidene))bis(azanylylidene))bis(methylene))bis(2-hydroxy-3,1-phenylene))bis(methylene))bis(1-(3-formyl-2-hydroxybenzyl)-1*H*-benzo[*d*]imidazol-3-ium) chloride Scheme 6 Synthesis of 2c SO₃H sō₄н 1c2c нń Acetic acid HO<sub>3</sub>S sŌ₄H Reflux 1 h CI 6 1 8 он HOas ЧH òн sō₄н нс нó sō₄н HO<sub>2</sub>S SO<sub>3</sub>H т Л sō₄н но₃ѕ́ sō₄н SO<sub>3</sub>H он sō₄н CI sō₄н HO<sub>3</sub>S **∏**∶NH ΗN sŌ₄H ΞN HOas ÒН sŌ₄H он HO₃S SO<sub>3</sub>H HO<sub>3</sub>S ЧĽ sŌ₄H sō₄н Chemical Formula: C<sub>202</sub>H<sub>248</sub>Cl<sub>2</sub>N<sub>32</sub>O<sub>94</sub>S<sub>24</sub> Molecular Weight: 5468.68

## Scheme 7 Synthesis of Photocatalyst (SAFPTILM)

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Fig.1<sup>1</sup>H NMR Spectrum of Synthesis of SAFPTILM (Photocatalyst)

In a 100 mL RBF, the precursors (1c) (4.03 g, 6 mmol) and (2c) (0.875 g, 1 mmol) were weighed, mixed with 25 mL acetic acid and stirred for 10 min. To this, pyrrole (0.536 g, 8 mmol) was added and the reaction mixture continued for stirring at room temperature for 1 h. The desired dark brown solid SAFPTILM was separated by vacuum filtration, rinsed with water (5 x 15 mL) to remove traces of acetic acid. Finally the product was frequently washed with acetone and dried in oven at 80°C to

furnish the SAFPTILM photocatalyst.<sup>34</sup> Yield: 90 %, 4.52 g.

<sup>1</sup>H NMR (400MHz, DMSO)  $\delta$  = 9.63 (s, 10H), 8.94 (s, 12H), 7.34 (s, 6H), 7.29 (s, 4H), 7.19 (s, 2H), 7.03 (s, 5H), 6.69 (s, 5H), 6.66 (s, 2H), 6.33 (s, 13H), 6.19 (d, 20H), 5.71 (d, 29H), 5.45 (d, 3H), 4.06 (s, 16H), 3.17 (t, 26H), 1.97 (t, 24H), 1.57 (s, 8H), 1.43 (s, 8H), 1.21 (s, 13H), 0.76 (d, 16H), 0.45 (t, 22H), -0.099 (s, 4H).

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## Combine process for the synthesis of photocatalyst (SAFPTILM)

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#### 3. Results and discussion



**Fig. 2** Comparative FT-IR spectra of chloroacetylated product (1c), (2c) and photocatalyst

A series of Infrared spectra were recorded to confirm the formation of SAFPTILM photocatalyst from pyrrole, 1c and 2c. In the spectrum 1c (Fig. 2) the band near 3346.50 cm<sup>-1</sup> was attributed to the hydroxyl group.<sup>35</sup> The appearance of intense peaks at 1598.99 cm<sup>-1</sup> was interpreted as an aromatic aldehyde.<sup>36</sup> In addition, relatively intense IR peaks at 1180.44 cm<sup>-1</sup> was exhibited due to SO<sub>3</sub> groups<sup>37</sup> while the bands appeared at 1516.05 cm<sup>-1</sup> and 1180.44 cm<sup>-1</sup> are the distinctive bands of C=N and C-N respectively, evidenced the formation of 1c.<sup>38</sup> A very intense peak at 3535.52 cm<sup>-1</sup> is assigned to hydroxyl groups in 2c. Another strong one is found View Article Online DOI: 10.1039/D0NJ03637D

at 1707 cm<sup>-1</sup> that originated due to stretching of aromatic aldehyde groups of 2c. Moreover, the appearance of peak at 3055.24 cm<sup>-1</sup>, more intense peak at 1533.41 cm<sup>-1</sup>, 1340.53 cm<sup>-1</sup> and 1145.72 cm<sup>-1</sup> attributed to C-H, C=N, C=C and C-N stretching respectively.<sup>39</sup> It was reported that there was no intense stretching band due to SO<sub>3</sub> in 2c.

The spectrum of photocatalyst displays a broad absorption peaks at 3200 to 3500 cm<sup>-1</sup> attributed to amino ((N-H), and hydroxyl (-OH) groups, but it less intense in 1c and 2c. Also, an additional band emerges near 1589.34 cm<sup>-1</sup> was the characteristic of C-C vibration of the phenyl substituents at mesoposition of porphyrin rings, indicating the formation of SAFPTILM and do not reflected in the IR spectra of substrates. The absorption bands in the region of 3000-2800 cm<sup>-1</sup> are designated to aromatic C-H stretching.40 The formation of photocatalyst was further supported by the appearance of intense band of symmetric stretching of SO<sub>3</sub> at 1103.28 cm<sup>-1</sup> and very weak intense band at 605.65 cm<sup>-1</sup> due to wagging of the CH and NH bonds. All the compounds 1c, 2c and photocatalyst SAFPTILM were further confirmed by FT-NMR studies.<sup>41</sup>



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Fig.3 N<sub>2</sub> isotherm of SAFPTILM

The pore size and pore volume of SAFPTILM photcatalyst were measured from the N<sub>2</sub> adsorption/desorption isotherms, using an Autosorb IQ Surface Area Gas Sorption Analyzer. It can be seen from the  $N_2$  adsorption-desorption isotherm that synthesized photo-catalyst can be recognized to type II (or type IV), which suggests a microporous pore texture.<sup>42</sup> (Fig. 3) Furthermore, from the isotherms of photo-catalyst, it is apparent that the total surface area of photo-catalyst and pore width is found to be 125 m<sup>2</sup>/g and 8.440 Å respectively, which is comparatively larger than the reported photo-catalyst. Moreover the surface area of the photo-catalyst will be more vital for effective catalysis.43



The characterization of the optical properties of the photocatalyst needs the use of diffuse reflectance spectroscopy (DRS) to know the optical bandgap of SAFPTILM from a Tauc plot<sup>44</sup> (Fig. 4) showed the UV-vis DRS spectra, indicating band gap of SAFPTILM photocatalyst by the intercept of tangents to the plots of (ahv)<sup>1/2</sup> versus photo energy is 1.55 eV.<sup>45</sup> This is associated with the strong absorption characteristics of SAFPTILM in the visible region accelerating photocatalytic activity at normal temperature under visible light irradiations.





The thermal stability of the SAFPTILM was studied by thermo gravimetric analysis (TGA), as illustrated in (Fig. 5) The TGA disclosed that the catalyst follows three-step degradation patterns.<sup>46</sup> The first weight loss 10.40 % below 209 °C may be due to physisorbed water. The second weight loss 41.09 % in the range 209–517 °C due to collapse of the meso-phenyl group by decomposition of -OH/ benzimidazoles groups. Furthermore, the weight loss above 517 °C may be due to decomposition of

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porphyrin scaffold. The TGA results confirmed that the catalyst is stable up to 517 °C and applicable for high-temperature reaction.<sup>47</sup>



Fig.6 SEM/EDX image of SAFPTILM

The SAFPTILM photocatalyst was analysed by SEM-EDX to investigate surface morphology and elemental composition (Fig. 6). The SEM image displays active surfaces, which would be favourable for photocatalytic properties to absorb light. Moreover elemental analysis showed all the expected elements in the photocatalyst with their composition as 71.12% measured as C, while the next is 18.89% of O, 4.42% of N, 2.90% of Cl and 2.65% of S by weight.<sup>48</sup>



Fig.7 Hammett acidity spectra of photo-catalyst

Acidity is important aspect to assess reactivity of heterogeneous photo-catalyst. The Hammett acidity function (H<sub>0</sub>) as an indicator for ranking the solid acid catalysts<sup>49</sup>. The strength of acidic catalyst can determine by (H<sub>0</sub>) Hammett function. pKa values obtained for SAFPTILM (photocatalyst) using Hammett indicators. Visual or spectrophotometric observation of the colour change of an adsorbed indicator supports in the assessment of the basic or acid strength of the surface. Hammett indicators are uncharged bases that can give up the proton and transformed to conjugate acids. As per literature, acidity of photo-catalyst was determined using UV-visible spectrophotometer with a basic indicator by adapting the concept reported in literature.<sup>50</sup> In the present work, H<sub>0</sub> values of SAFPTILM photo-catalyst was determined using 10 PPM of 4-nitroaniline (50 mL) as the indicator, with 100 mg photo-catalyst. The maximum absorbance of the unprotonated form of the basic indicator in water was observed at 370 nm, attests increase in acidity of the photo-catalyst, whereas the protonated form of the indicator could not be observed because of its small molar absorptivity and its location. Thus, the ratio [I]/[IH<sup>+</sup>] was determined from the differences of measured absorbance after the addition of photo-catalyst and the relative acidity was calculated by using Eq. (1) as a Hammett function

 $(H_0) = pK(I)aq + log(I/IH^+)....(1)$ 

Hammett values (H<sub>0</sub>) of the SAFPTILM photocatalyst was found to be H<sub>0</sub> = 0.72 and correlated with their catalytic activity (Fig. 7). The catalytic activity was enhanced with the acidity of the photocatalyst which reveals the formation of hydrogen bonding of photo-catalyst to the substrate and this could play a crucial role to facilitate the product formation.

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#### 4. Heck Coupling



#### Scheme 8

Synthesisof(E)3(4aminophenyl)acrylonitrile

4-chloroaniline (30 mmol, 3.82 gm), acrylonitrile (32 mmol, 1.59 gm), photocatalyst SAFPTILM (20 mg), 5W yellow light, 18 h

Subsequently, catalytic performance of SAFPTILM was explored in the valuable carbon-carbon bond formation via coupling reactions. We have verified our research by considering Mizoroki-Heck coupling reaction, a reaction of 4-chloroaniline (30 mmol, 3.82 gm) and acrylonitrile (32 mmol, 1.59 gm) as a model reaction, using 20 mg photocatalyst for 18 h in home-made photoreactor at an ambient temperature.<sup>51</sup> The reaction mixture was extracted with ethyl acetate, the catalyst was separated by filtration. The desired product was obtained by evaporation of the solvent with rotavapour and purified by recrystallization using suitable solvent. (Entry 1, Table 1) The formation of product was observed in absence of any solvent/base and confirmed from spectral analysis (Figure S12 to Figure S33, supporting file). Then, we have scrutinized the reaction conditions by changing the different reaction factors and the results are summarized in Table 1.

As catalyst quantity in a reaction primarily decides the catalytic efficiency, the catalyst loading required for effective transformation was the first parameter selected and studied. The yield of C-C product was found to increase with the increase in the amount of catalyst used from 5 mgvto 20 mga DOI: 10.1039/DONJ03637D (Figure S8 supporting Information) However, the yield of the product did not alter using 25 mg photocatalyst, may be due to accumulation of photocatalyst.<sup>52</sup> (Entry 2-6, Table 1). Thus, 20 mg quantity was evidenced as the optimum loading of SAFPTILM photocatalyst.

Likewise, the yield of Heck product firmly depends on the duration of reaction. This was examined by analysing the model reaction at different intervals of time. The rate of product formation was enhanced till the completion at 18 h, beyond which amount of conversion remained nearly insignificant. (Entries 7-10, Table 1). This steered to select optimal reaction time for C-C coupling as 18 h.

Next we explored the impact of light intensity and wavelength in the Mizoroki-Heck reaction. As shown in Table 1 comparable yield of the product was obtained in lesser duration (Entries 11-12) showing better performance of the catalytic system, when the intensity of light was increased by using 9 W (Yield 87 %, 15 h) and 12 W (Yield 90 %, 13 h) LED light with other reaction conditions unchanged. Thus, there is a progressive relationship between the reaction rate and the light intensity.<sup>53,54</sup> Similar results were also perceived when wavelength of visible light changed to green (Table 1, entry 13) (480 nm) and Solar radiations using optimized reaction conditions (Table 1, entry 14). It was also confirmed that reaction does not proceed in the dark using optimized reaction parameters (Table 1, entries 15). Thus, 20 mg of photocatalyst for 4-chloroaniline (30 mmol, 3.82 gm) and acrylonitrile (32 mmol, 1.59 gm) under 5 W LED in home-made photoreactor was established as optimized reaction parameters for model Heck coupling reaction.

Using these optimized reaction conditions, we explored the general applicability of BAFPBM

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photocatalyst with different aryl chlorides and vinyl **Table 1** Optimization of Heck Coupling View Article Online substituents containing electron withdrawing or Entry Reagent Catalyst Time donating groups (Table 2). The BAFPBM catalysed Mizoroki-Heck reaction tolerated an extensive range of functional groups such as NO<sub>2</sub>, Cl, OH and NH<sub>2</sub>. The unactivated aryl chlorides and substituted vinyl compounds demonstrated excellent reactivity without using any noble metal and base and afford expected products in high yields under optimized reactions conditions. (Table 2, entries 1-11). Additionally, heterocyclic aryl chlorides like 2chloro thiophene and 2-chloro-pyrimidine and substituted vinyl compounds also confirmed admirable reactivity in absence of any noble metal and base with moderate to excellent yields under optimized reactions conditions. (Table 2, entries 12-14). Similarly, heterocyclic vinyl pyrimidine and thiophene also delivered Heck products with substituted aryl chlorides. (Table 2, entries 15-16). Finally both the heterocyclic substrates were also investigated in our present system rendering 83 % of coupling product. (Table 2, entry 17).

## Model reaction of Heck Coupling



Linery	neugene	catalyst	Time	illeid
	(*)	(mg)	(h)	(%)
1	R1 +R2	20	24	89
2	R1 +R2	5	24	54
3	R1 +R2	10	24	68
4	R1 +R2	15	24	76
5	R1 +R2	20	24	89
6	R1 +R2	25	24	90
7	R1 +R2	20	6	61
8	R1 +R2	20	12	70
9	R1 +R2	20	18	88
10	R1 +R2	20	24	89
11	R1 +R2	20	15	87ª
12	R1 +R2	20	13	90 <sup>b</sup>
13	R1 +R2	20	18	89°
14	R1 +R2	20	18	92 <sup>d</sup>
15	R1 +R2	20	18	5 <sup>e</sup>

\*=5W yellow light; (0.004 w/cm<sup>2</sup>)

a=9W light ; b= 12 W light ; c= 5W Green light; d= Solar light;

e= reaction performed in dark

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Yield

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## View Article Online **Table 2** Heck coupling between various Aryl Halides and Activated Alkene under Photocatalytic Condition

Sr. No.	Alkene	Aryl Halide	Product	Time h	Yield %
1	CN	H <sub>2</sub> N Cl	NC-NH2	18	88
2	Br	O <sub>2</sub> N CI	O <sub>2</sub> N Br	18	86
3	<i>∕∕</i> <sup>Br</sup>	0 CI	Br	18	86
4	//NH <sub>2</sub>	O <sub>2</sub> N Cl	O <sub>2</sub> N NH <sub>2</sub>	18	82
5	∕он	0 Cl	0°CO-OH	18	84
6	∕o∕o	O <sub>2</sub> N	O <sub>2</sub> N O	18	84
7	200			18	81
8	<i>™</i> °∕			18	88
9		0 CI	o o o	18	85
10	$\frown$	0 CI	0	18	87
11		Cla	C)_/_C)_CI	18	81
12	<i>∕∕</i> Br	С	Br	18	85

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Reaction conditions: aryl halide (30 mmol, 3.82 gm), activated alkene (32 mmol, 1.59 gm), photocatalyst SAFPTILM (20 mg), 5W yellow light, 18 h (Table 2).

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**Table 3** <sup>1</sup>H and <sup>13</sup>C value for Heck coupling between various Aryl Halides and Activated Alkene under Photocatalytic Conditions.

Heck Coupling product	Conformation Data (NMR data)
	<ul> <li><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ : δ 8.20 (d, 2H), 8.18 (d, 2H), 7.53 (d, 1H), 7.51 (d, 1H), 1.55 (s, 3H)</li> <li><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 170.1, 150.3, 142.2, 135.2, 132.0, 125.2, 113.0, 25.1 GC-MS: 207.19</li> </ul>
NC NH <sub>2</sub>	<ul> <li><sup>1</sup>H NMR (400 MHz, DMSO-d6): δ 7.95 (d, 2H), 6.71 (s, 1H), 6.61 (s, 2H), 6.58 (s, 1H), 5.75 (s, 2H)</li> <li><sup>13</sup>C NMR (100 MHz, DMSO-d6): δ 99.7, 112.84, 126.86, 136.08, 156.16 GC-MS: 144.18</li> </ul>
	<sup>1</sup> H NMR (400 MHz, DMSO-d6): δ 10.01 (s, 1H), 7.95 (t, 2H), 7.70 (d, 2H), 7.57 (d, 2H), 2.86 (s, 2H) <sup>13</sup> C NMR (100 MHz, DMSO-d6): δ 166.92, 138.25, 131.65, 131.61, 130.12, 129.85, 129.21, 40.2 GC-MS: 225.09
En un de la construction de la cons	<sup>1</sup> H NMR (400 MHz, DMSO-d6): δ 10.01 (s, 1H), 7.93 (t, 2H), 7.69 (d, 2H), 7.57 (d, 2H), 4.07 (q, 2H), 36.36 (t, 3H). <sup>13</sup> C NMR (100 MHz, DMSO-d6): δ 192.62, 139.40, 135.31, 131.65, 129.84, 129.21, 70.4, 20.2 GC-MS: 204.23
an a	<ul> <li><sup>1</sup>H NMR (400 MHz, DMSO-d6): δ 8.47 (d, 2H), 8.25 (d, 2H), 7.76 (s, 1H), 7.74 (s, 1H), 4.38 (t, 2H), 1.22 (s, 2H)</li> <li><sup>13</sup>C NMR (100 MHz, DMSO-d6): δ 146.87, 140.64, 130.33, 125.80, 50.2 GC-MS: 178.19</li> </ul>
	$^{1}\text{H}$ NMR (400 MHz, CDCl <sub>3</sub> ) $\delta$ : $\delta$ 8.66 (d, 2H), 7.53 (d, 1H), 7.31 (t, 1H), 7.11 (d, 1H) $^{13}\text{C}$ NMR (100 MHz, CDCl <sub>3</sub> ) $\delta$ : 161.69, 159.86, 159.60, 120.01, 119.7, 105.2 GC-MS: 130.15
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) δ :δ 8.19 (d, 2H), 8.18 (d, 2H), 7.53 (d, 1H), 7.51 (t, 1H), 1.59 (s, 1H) <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ) δ: 146.55, 141.38, 129.58, 125.18, 124.93, 25.2 GC-MS: 242.07

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	<ul> <li><sup>1</sup>H NMR (400 MHz, DMSO-d6): δ 8.77 (d, 2H), 8.52 (5) (2015)</li> <li>7.56 (t, 1H), 7.46 (s, 1H), 6.74 (t, 1H), 6.12 (d, 1H), 5.54 (d, 1H)</li> <li><sup>13</sup>C NMR (100 MHz, DMSO-d6): δ 171, 160.698, 160.65, 149.99, 134.92, 121.33, 120.22</li> </ul>
	<ul> <li><sup>1</sup>H NMR (400 MHz, DMSO-d6): δ 10.26 (s, 1H), 7.76 (q, 2H), 7.61 (t, 3H), 7.50 (d, 1H), 7.45 (t, 1H).</li> <li><sup>13</sup>C NMR (100 MHz, DMSO-d6): δ 190.12, 136.75, 136.07, 132.39, 131.03, 129.98, 128.16</li> </ul>
för ander andere an ander andere a	<ul> <li><sup>1</sup>H NMR (400 MHz, DMSO-d6): δ 9.97 (s, 1H), 7.91 (d, 2H), 7.65 (d, 2H), 5.91 (d, 2H), 5.56 (s, 1H), 5.26 (d, 1H), 5.13 (d, 1H).</li> <li><sup>13</sup>C NMR (100 MHz, DMSO-d6): δ 192.67, 139.90, 135.23, 131.63, 129.80, 129.14, 128.82, 128.68, 117, 66.74</li> </ul>
	<ul> <li><sup>1</sup>H NMR (400 MHz, DMSO-d6): δ 8.23 (s, 4H), 7.47 (d, 2H), 7.39 (d, 3H), 5.84 (d, 1H), 5.29 (d, 1H), 4.72 (s, 2H).</li> <li><sup>13</sup>C NMR (100 MHz, DMSO-d6): δ 139.67, 138, 125.22, 125.24, 125.21, 125.20, 125.18, 45.2</li> </ul>
	<sup>1</sup> H NMR (400 MHz, CDCl <sub>3</sub> ) : δ 10.49 (s, 1H), 8.49 (q, 2H), 7.51 (q, 1H), 7.30 (t, 3H), 7.00 (s, 1H), 6.11 (s, 1H), 5.69 (s, 1H), 5.49 (d, 1H). <sup>13</sup> C NMR (100 MHz, CDCl <sub>3</sub> ) : δ 206.97, 149.95, 149.71, 147.10, 138.83, 133.12, 130.62, 129.63, 129.27, 128.37, 127.18, 121.41, 120.80, 118.78, 117.59
0-0-0	<ul> <li><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ 9.98 (s, 1H), 7.83 (d, 3H), 7.82 (d, 2H), 7.52 (t, 2H), 7.51 (d, 2H), 7.42 (s, 2H).</li> <li><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) : δ 190.86, 140.98, 134.73, 131.52, 130.91, 129.47, 128.83, 128.05. GC-MS: 208.26</li> </ul>
	<ul> <li><sup>1</sup>H NMR (400 MHz, DMSO-d6): δ 10.16 (s, 1H), 9.98 (s, 1H), 7.30 (d, 1H), 7.12 (t, 4H), 6.98 (d, 1H), 6.77 (q, 3H).</li> <li><sup>13</sup>C NMR (100 MHz, DMSO-d6): δ 192.42, 170.79, 153.54, 130.28, 129.99, 129.76, 128.99, 128.83, 128.67, 128.40, 128.11, 120.66, 120.41, 120.14, 117.42</li> <li>GC-MS: 225.25</li> </ul>
	<ul> <li><sup>1</sup>H NMR (400 MHz, DMSO-d6): δ 9.98 (s, 1H), 8.00 (d, 2H), 7.42 (t, 4H), 7.31 (q, 2H), 7.10 (d, 1H), 6.76 (s, 1H).</li> <li><sup>13</sup>C NMR (100 MHz, DMSO-d6): δ 192.10, 164.95, 135.27, 135.01, 133.52, 133.49, 132.87, 132.77, 132.50, 132.32, 132.23, 132.04, 131.94, 131.61, 116.91</li> </ul>

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**Fig.8** FT-IR for Confirmation of Recyclability and Stability of Photocatalyst



**Fig.9** Recyclability and Stability of Photocatalyst

#### **Recyclability and Stability of Photocatalyst**

In order to know practical utility and efficiency of heterogeneous SAFPTILM photocatalyst, reusability of photocatalyst has been evaluated by performing Heck coupling using 4chloroaniline and acrylonitrile as the substrate under optimized conditions. After the completion of photocatalytic reaction, the reaction mixture was allowed to settle for 10 min, and the catalyst was separated by simple filtration, washed with ethyl acetate (2x10 ml), finally with acetone and dried in hot air oven. The recovered SAFPTILM photocatalyst was use again for the next cycle by charging substrates. The catalyst demonstrated excellent stability and reusability with slight reduction of yield of the product for six cycles (reduced yield from 88 to 82%) (Fig. 9). The Fourier Transform Infrared spectroscopy (FT-IR) measurements were carried out for the Photocatalyst, recovered after sixth cycle. It was found that FT-IR bands were in good agreement with original spectra of the fresh Photocatalyst (Fig. 8 FT-IR). Therefore, the SAFPTILM is found to be more appropriate as heterogeneous photocatalyst for C-C coupling reactions under visible light irradiation at ambient conditions.

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Scheme 9 Proposed mechanism to explain the role of scavenger (p-BQ and EDTA) in Heck Coupling

reaction.



Fig.10 Photocatalytic Heck coupling of Aryl chloride with acrylonitrile in presence of p-benzoquinone (electron scavenger) and EDTA (hole scavenger)

It is identified that the electrons and holes are the important active species generated during the photocatalytic reaction. Benzoquinone and EDTA, the scavengers of electrons and holes, respectively, can be added to investigate the photocatalytic pathway. As shown in Fig. 10, the formation of desired product of Heck coupling found with 88 % yield, while the percentage of yield decreased intensely after adding benzoguinone and EDTA. These results verified that the electrons and the holes were dynamic species, for the C-C coupling by the formation of alkoxy radicals and phenyl radicals reepectively as shown in the mechanism.





Scheme 10. Plausible mechanism of C-C Heck coupling using SAFPTILM Photocatalyst

A wide-range of cross coupling reactions have been developed, involving transition metal catalysts between prefunctionalized reactants and an arene or C-H arylation through functionalization in one coupling substrate.

However, there is aggravation among the researchers that such coupling reactions always need high temperature and excessive equivalent of bases/additives than the substrates. Hence, photoredox catalysis that

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harness light energy under mild conditions to accelerate arylation by single electron transfer, has becoming popular over the past decade. A wide range of aryl radical precursors, have been reported, that lead to formation of aryl radical during photocatalysis to enable C-C, C-N, C-S cross coupling reactions. For example, aryl salts diazonium for C-H arylation of heteroarenes<sup>55,56</sup> diaryliodonium salts for arylation of heteroarenes and olefins<sup>57,58</sup> and triaryl sulfonium salts reported for the generation aryl radicals under visible light irradiations to afford allylation products.<sup>59</sup> Recently, Fazhi et al. have successfully demonstrated a novel and reliable approach for the conversion of aryl halides to aryl radical using a super electron donor, rongalite in absence of transition metal.<sup>60</sup> Among the reported aryl radical precursors, aryl halides have attracted global attention for the generation of aryl radicals, due to easy availability, inexpensive and stability at normal conditions. But the access of aryl halides as precursors for the generation of aryl radical is often restricted due to high reduction potential (> -2.0 V) and high bond dissociation energy (>97 kcal/mol) and resistant to single electron reductions. To surpass this obstacle, the research group of de Alaniz<sup>61</sup> has demonstrated generation of aryl radical by using 10phenylphenothiazine (PTH) as photocatalyst under UV light irradiation (380 nm). The negative reduction potential of excited PTH afforded aryl radicals from aryl halides with electron donating groups. Further, aryl radicals have generated using the excited doublet states of stable radical anions, by in situ formation photoinduced through electron transfer processes.<sup>62</sup>

#### Studies have shown that, photostable organic dye, perylene bisimides form stable and coloured radical anions under nitrogen atmosphere.63,64 Similar this, to the photocatalytic performance of SAFPTILM photocatalyst was excellent with all cross coupling and C-H activation under visible light irradiation at ambient conditions in absence of noble metal and base (Scheme 9). This may be due to presence of ionic liquid based triazolium moiety to acquire basic character and sulfonic acid groups on the periphery provide strong SAFPTILM electron donor centres in photocatalyst. The probable mechanism for C-C, C-N coupling and C-H activation involve following steps upon visible light irradiation:

[A] Excitation of photocatalyst SAFPTILM by absorption of visible light to form SAFPTILM<sup>\*</sup>.

[B] Photoexcited SAFPTILM<sup>\*</sup> extracts an electron from electron donor group (-SO<sub>3</sub>H) lead to radical anion (SAFPTILM<sup>•-</sup>) in the ground state.

[C] The transfer of an electron from a stable SAFPTILM<sup>•-</sup> by sequential photoexcitation to aryl chlorides, creating the aryl radical precursor ArCl<sup>•-</sup> and regeneration of neutral SAFPTILM.

[D] The formation of an active intermediate, aryl radical (Ar\*) by breakup of ArCl\*-

[E] The photogenerated holes on the SAFPTILM photocatalyst could oxidize vinyl cyanide to vinyl cyanide radical and protons.<sup>65,66</sup>

The aryl radical and vinyl cyanide radical coupled quickly to attain C-C coupled product while the proton and chloride ion lead to form HCl byproduct (Scheme 9).

#### View Article Online DOI: 10.1039/D0NJ03637D



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4-chloroaniline (30 mmol, 3.82 gm), phenyl acetylene (30 mmol, 3.06 g), photocatalyst SAFPTILM (20 mg), 5W yellow light, 24 h

Encouraged by the catalytic performance and stability of SAFPTILM in Mizoroki-Heck coupling reactions, we have established its efficacy in one more significant C-C bond involving reaction by Sonogashira coupling. It is primarily used in the synthesis of biaryl compounds, by coupling of a terminal alkyne and an aryl halide in presence of a palladium catalyst along with copper co-catalyst. Here, we have optimized Sonogashira coupling between 4-chloroaniline and phenyl acetylene using SAFPTILM photocatalyst. It was found that only 20 mg of SAFPTILM was necessary to catalyse Sonogashira coupling of 4-chloroaniline (30 mmol, 3.82 g) and phenyl acetylene (30 mmol, 3.06 g) under visible light irradiation (5 W LED) in absence of noble metal in 15 ml of methanol in 24 h with 96% of the biphenyl (Scheme 10). The coupling of aryl chlorides with deactivating and activating groups carried out with phenyl acetylene under optimized reaction conditions to achieve good to

excellent yields of biaryl compounds (Table 4 entries 1-5). The details of optimization protocols were tabulated in (Table 3 Supporting Information). The SAFPTILM photocatalyst was capable to delivered Sonogashira products in methanol under visible light irradiation at ambient conditions in home-made photocatalytic reactor. Differently substituted aryl chlorides electron donating and withdrawing, including heterocyclic ring were also contributed in this C-C coupling reaction without any effort. The catalyst was separated, filtered and reused up to 4 times following the procedure as illustrated previously and results were incorporated in the supportive information (Fig. S42 Supporting Information).

Sr. No	Activated Alkyne	Aryl Halide	Product	Time	Yield
1		NH <sub>2</sub>		24	<u>96</u>
2		OH	OH OH	24	79
3			$ \begin{array}{   } \hline \\ \hline \\ \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	24	78
4				24	62
5			= - = - = - + = - = -	24	72

 Table 4 Sonogashira coupling between various Ethynylbenzene and Aryl halide under Photocatalytic

 Conditions.

Reaction conditions: aryl halide (30 mmol, 3.82 gm), phenyl acetylene (30 mmol, 3.06 g), photocatalyst SAFPTILM (20 mg), 5W yellow light, 24 h.

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#### 6. Buchwald-Hartwig Cross Coupling Reaction





4-chloroaniline (30 mmol, 3.82 gm), 1H-pyrrole (30 mmol, 2.01 gm), photocatalyst SAFPTILM (20 mg), 5W yellow light, 18 h

Next, we have tested prospective of SAFPTILM photocatalyst in industrially important Buchwald C-N cross coupling reaction. The Buchwald-Hartwig amination is a C-N the cross coupling reaction of amines and aryl or heteroaryl-halides in presence of Pd and base to achieve aryl amines or heteroaryl amines. The reaction has acquired extensive applications in synthetic organic chemistry, particularly pharmaceuticals<sup>67</sup> and other industrial applications involving  $\alpha$ -arylation of carbonyl compounds and nitriles.<sup>68</sup> However, in addition to argon protected atmosphere, Buchwald C-N coupling shows, incompatibility of some groups like nitro, ester of substrate with strong bases of the reaction medium and poisoning/leaching of Pd catalyst are the major restrictions. To address these drawbacks of existing catalysts, the scope of current protocol has been investigated, to justify the requirement of industries. When a mixture of 4chloroaniline (30 mmol), pyrrole (30 mmol), and 20 mg photocatalyst was irradiated under visible light in home-made photoreactor at ambient

condition in absence of any solvent/base/noble metal, appreciable yield (87%) of N-substituted

pyrrole was obtained (Scheme 11). Like other protocols, the rate of reaction was significantly enhanced with change of light intensity and wavelength (Fig. S10 & Fig. S11 Supporting file) with excellent yield of desired products. A variety of aryl chlorides coupled with pyrrole to attain Nsubstituted heterocyclic compounds in good yields under optimized reactions conditions. (Table T5 Supporting file). The results were summarized in Table 5 Aryl chlorides comprising both electron donating groups (-NH<sub>2</sub>, OCH<sub>3</sub>) and electron withdrawing groups (-NO<sub>2</sub>, CHO) were contributed in the Buchwald coupling reactions. The results indicated that many electronically varied aryl halides tolerated using the current protocol (Table 5)

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**Table 5** Formation of C-N bond between various Aryl halide, Pyrrole and Morpholine under PhotocatalyticConditions.

Sr. No	Aryl Halide	Substrates with NH	Product	Time h	Yield %
1	NH <sub>2</sub>	HN	H <sub>2</sub> N	18	87
2	OCH <sub>3</sub>	HN	H <sub>3</sub> CO	18	82
3		HN	O <sub>2</sub> N	18	72
4	NO <sub>2</sub> Br	HN		18	77
5	O CI	HN		18	74
6			O <sub>2</sub> N O	18	72

Reaction conditions: aryl halide (30 mmol, 4.21 gm), Substrates with NH (30 mmol, 2.01 gm), photocatalyst SAFPTILM (20 mg), 5W yellow light, 18 h

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#### Scheme 13 Synthesis of benzidine

4-chloroaniline (30 mmol, 3.82 gm), photocatalyst SAFPTILM (20 mg), 5W yellow light, 16 h

One more rationally and industrially essential reaction is the coupling of sp2-sp2 C-C coupling to form biaryl compounds either by like Ullmann or Fittig type reactions. The synthesis of biaryl in presence of copper catalyst is well-known to attain C-C bond in organic compounds. The formation of symmetrical and unsymmetrical aryl-aryl bond is one of the most important goals to synthesize precursors and intermediates required in agrochemical, pharmaceutical and fine chemical industries. In spite of the impressive achievement in the copper catalysed biaryl formation, there still exists a need for new approaches that eliminate use of strong bases, high temperature; long duration and adapting cheap and environmentally benign catalysts operating at normal conditionsThus, synthetic approaches like metal-, ligand-, and additive free conditions, reusable heterogenous

catalysts, photocatalytic, microwaveand ultrasound assisted synthesis, etc. have attracted to afford biaryl compounds.<sup>69,70</sup>. Thus, different of aryl halides including unactivated and activated aryl chlorides were coupled themselves to produce corresponding substituted diaryl compounds in good yields using optimized parameters under visible light irradiations (See SI Table S9). The results are indicated in Table 6. Aryl chlorides with deactivating groups (-NH<sub>2</sub>) and activating groups (such as -NO<sub>2</sub>, CHO) were involved in the formation of respective Ullmann/Fittig biaryl products. The yields of the product found better in the substrate containing activating groups like NH<sub>2</sub> compare to deactivating group like CHO, NO<sub>2</sub> in the coupling reactions. It is remarkable that Ullmann type biaryl formation reactions required copper as co-catalyst and amine/Na or K t-butoxide as base in which are poisonous in nature. But, in this approach the C-C coupling reactions were afforded in visible light

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radiation under copper and amine-free at ambient acetone, dried in hot air oven and recycled for ADOI: 10.1039/DONJ03637D conditions with appreciable yields. Moreover SAFPTILM photocatalyst was separated after completion of reaction by filtration, washed with

times.

## Table 6 Ullmann coupling product under Photocatalytic Conditions.

Sr. No	Aryl Halide	Aryl Halide	Product	Time h	Yield %
1	NH <sub>2</sub> CI	NH <sub>2</sub>	H <sub>2</sub> N-\NH <sub>2</sub>	16	91
2	CI	C		16	91
3	O CI			16	82
4				16	74

Reaction conditions: aryl halide (30 mmol, 3.37 gm), photocatalyst SAFPTILM (20 mg), 5W yellow light, 16 h

in C-H activation, that can used for the synthesis of substrate prefunctionalization such as halogenation, borylation, metalation etc. Here, we chloroaniline and 1-naphthol using SAFPTILM photocatalyst. It was found that 20 mg photocatalyst was enough to catalyze the reaction under visible light irradiation in 20 h with 76% desired product (Scheme 13). Different phenols underwent coupling with aryl chlorides under yields corresponding excellent of phenol derivatives (Table 7 entries 1,2 and 4). The spectral file). In contrast to single heterogeneous catalyst performing one reaction, all the above-mentioned reactions are entirely photocatalyst. This photocatalyst is preferred due reaction mixture reducing work up procedures, and possible to reduce the cost and consumption of solvent/noble-metal/base promote free reactions, replacing corrosive reagents and green chemistry.

(30 Naphthalen-1-ol mmol, 4.32 gm), 4chloroaniline (30 mmol, 3.82 gm), photocatalyst SAFPTILM (20 mg), 5W yellow light, 20 h

The word C-H activation involves transformation of carbon-hydrogen bond of substrates into carboncarbon or carbon-heteroatom bonds, using metal or metal complex as catalysts.71-73 The most common approach involve treatment of the C-H bond of one substrate with a carbon-halogen bond through (C-X) of other. organometallic intermediates (B, Sn, Zn, Mg, etc.). Transition metals have been established to react with C-H bonds to generate C-M bonds via C-H activation, that can be converted to a range of functional groups under mild conditions.<sup>74</sup> Besides, all the benefits, the use of C-H bonds as targets have two notable disadvantages. The first one is the inert nature of C-H bond and another one is the selectivity of C-H in molecules containing multiple bonds. However, photocatalytic path could signify the perfect key for these drawbacks, as a photocatalyst is competent of activating the substrate via different mechanisms when in the excited state, like electron transfer or hydrogen atom transfer. The photocatalysts are known to induce a direct hydrogen atom transfer process, whereby excited photocatalyst initiates the process by homolytic cleavage of a C-H bond in organic compounds (R-H) including aldehydes, ketones, amides, esters, nitriles, alkyl aromatics, and alkanes etc.<sup>75-77</sup> Inspired by the versatile photocatalytic activity of SAFPTILM in C-C and C-N coupling reactions, finally we have examined its application

various targeted organic compounds eliminating have optimized C-H activation between 4optimized reaction conditions to attain good to data was summarized in (Table T6 supporting Information accomplished in the presence of a single SAFPTILM to its robustness, recyclability, easy recovery from lower operational cost. Additionally, it may be various precursors required during the synthesis of catalysts, leading to lower both financial and environmental stress on the industry. These desired characteristics reflected in this manner contribute to aggressive oxidants, attaining many principal of

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**Table 7.** CH activation between various Aryl halide and phenolic compound under Photocatalytic Conditions.

Sr. No	Aryl Halide	Phenol derivatives	Product	Time h	Yield %
1		OH	OH NH2	20	78
2	C	OH	OH	20	79
3	CI	ОН	ОН	20	80
4	CI	NO <sub>2</sub>	NO <sub>2</sub>	20	81
5	CI	OH	OH	20	82

Reaction conditions: phenol derivatives (30 mmol, 4.32 gm), aryl halide (30 mmol, 3.37 gm), photocatalyst SAFPTILM (20 mg), 5W yellow light, 20 h

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**Table 8.** Comparison of photocatalytic activity of SAFPTILM with other reported catalysts<sup>10</sup> in C-C (Heck) coupling reactions.

Catalyst	Catalyst Amount mg	Base	Temp °C	Time	Light	Solvent	Yield %	Reference No.
NaO <sup>t</sup> Bu	15	Base NaO <sup>t</sup> Bu	50	40 min	UV	H <sub>2</sub> O	77 %	[78]
Fe <sub>3</sub> Pd <sub>2</sub> (OH) <sub>2</sub> [picolinic acid] <sub>8</sub> (H <sub>2</sub> O) <sub>4</sub> Hybrid Nanorods	5	Et₃N	110	1.5 h	-	DMF	93 %	[79]
MP@Void-Pd@mSiO <sub>2</sub>	10	Et₃N	120	3 h	-	DMF	98 %	[80]
Nano Co	6.8	K <sub>2</sub> CO <sub>3</sub>	120	7 h	-	NMP	74 %	[81]
supramolecular polymer 4: Au NPs)	750	K <sub>2</sub> CO <sub>3</sub>	No	10 h	Visible	DMSO/ H <sub>2</sub> O	57 %	[82]
Photocatalyst (SAFPTILM)	0.67*	No	RT	18 h	Visible light	No	88 %	Our work

\*Catalyst loading for 1 mmol substrate (4-Chloroaniline), during optimization 30 mmol substrates used.

A comparison of photocatalytic performance of SAFPTILM with other catalysts for Mizoroki-Heck coupling is shown in Table 8 It is evidence from the results that. the SAFPTILM photocatalvst established a better or analogous, in photocatalytic activity than the other photocatalysts. The crucial advantages of the protocol are: Ambient reaction conditions, excitation of photocatalyst using visible light irradiations, very low band gap, moderate to excellent yield, lower catalyst loading (0.67 mg per mmol of substrate), tolerating activated and unactivated aryl chlorides and stability and recyclability.

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#### 4. CONCLUSIONS

We have successfully synthesized a heterogeneous photocatalyst containing Brønsted acid functionalized porphyrin entangled with triazolium moiety (SAFPTILM). The SAFPTILM photocatalyst was confirmed by FT-NMR, FT-IR and Scanning Electron Microscopy (SEM) coupled with energydispersive X-ray spectroscopy (EDS) for evaluating the surface morphology. The X-Ray Diffraction (XRD) and the Brunauer–Emmett–Teller (BET) analyses provided complementary information about the structure of photocatalyst. The surface acidity of the photocatalyst was determine by Hammett indicator, happened to match the activation process and proved by photocatalytic activity. Porphyrin is a bio-inspired tetrapyrrolic aromatic macrocyclic compound with massive conjugated system of 18 p-conjugated electronic systems, usually absorb intensely in the visible region of the electromagnetic spectrum. This conjugated network with the chromophore substituents on the meso-positions can provide rapid electronic conducting channels during photocatalysis.

The BAFPBM photocatalyst is proved to be an efficient photocatalyst for the Heck-Mizoroki coupling reaction of different aryl chlorides in absence of base/noble metal, under irradiation of visible light and also exceptionally effective for coupling of unactivated/activated aryl chlorides with phenyl acetylene (Sonogashira), pyrrole (N-H Buchwald-Hartwig), activation, phenols (C-H activation) and with other arvl chlorides (Ullmann/Fittig type) to achieve good to excellent yields of products in absence of base/noble metal under irradiation of visible light. The study reveals that highly effective and green photocatalytic protocols by which cross-coupling reactions, including Mizoroki-Heck, Sonogashira,

Ullmann/Fittig type, Buchwald-Hartwigkereactions DOI: 10.1039/DONJ03637D and C-H activation can be driven in home-made photo-reactor in presence of visible light (5 W LED) at ambient temperatures using SAFPTILM, thus achieving viable conditions. Unusually, high % yield of C-C, C-N coupled products were obtained by performing various reactions with aryl chlorides in absence of precious metals/bases/high temperatures adapting principle of green chemistry by avoiding work up to remove excess of bases.

The effect of light intensity was clearly observed when 5 W light replaced with 9W/12W light by decreasing duration in the formation of desired products due to the increased population of photoexcited electrons. The irradiation of different visible light wavelength also has a substantial influence on the reaction rates. The results reveal that the using yellow LED source considerably improves the yields of the reactions compare to green/blue/white LED light. Unusually, the electrons which are excited by the visible light can be transmitted to the conjugated benzimidazlium based phenylene diimine support that delays the recombination of photoinduced electron-hole pairs. [3087] photocatalyst validated excellent Moreover. stability and reusability with slight reduction of yield of the product for four cycles. The photocatalytic performance of SAFPTILM photocatalyst was excellent with all cross coupling and C-H activation under visible light irradiation at ambient conditions in absence of noble metal and base with the lowest catalyst loading 0.67 mg per mmol of substrate. This may be due to low band gap (1.55 eV), presence of ionic liquid based triazolium moiety to acquire basic character and sulfonic acid groups on the periphery provide strong electron donor centres in SAFPTILM photocatalyst. Further exploration of the photocatalyst for biomass transformation into value added compounds is under progress.

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## **AUTHORS INFORMATION**

<sup>#</sup>Karan Bhansali and Subodh Raut contributed equally, Shital Barange contributed for C-N <sup>13</sup> activation

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