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ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.8b00623 • Publication Date (Web): 12 Jun 2018 Downloaded from http://pubs.acs.org on June 12, 2018

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177x102mm (100 x 99 DPI)

# Natural sunlight driven oxidative homocoupling of amines by truxene based conjugated microporous polymer

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#### Abstract

In this study, we reported the synthesis of a metal-free Truxene based conjugated microporous polymer (Tx-CMP) and demonstrated heterogeneous photocatalytic application under direct sunlight. We employed Tx-CMP for the oxidative homocoupling of amines. This model reaction describes an effective way to harvest natural sunlight effectively for the organic transformations. The higher conversion and selectivity of Tx-CMP has been demonstrated with recyclability for at least 5 times without any decline in its catalytic activity under direct sunlight.

KEYWORDS: Truxene based CMP, Conjugated Microporous polymers, Heterogeneous photocatalysis, Amine homocoupling and Sunlight photocatalysis.

# Introduction

Natural sunlight is an abundant and inexpensive energy source which provides continues support to living beings in the form of food and biomass through photosynthesis.[1] Giacomo Ciamician, the father of organic photochemistry, had challenged the scientists to vision a chemical industry that can synthesize chemicals using sunlight resembling the photosynthesis in the plants.[2] Indeed, very few initial attempts of synthesising fine chemicals by homogeneous catalysis using organic dyes, metal complexes and simple organic molecules as photosensitizers proved that the fine chemical synthesis using solar energy is technically achievable and environmentally sustainable.[3] Despite of many efforts by researchers in the recent years using solar simulator in the laboratory, reactions in natural sunlight for organic conversion through heterogeneous catalysis is always a bottleneck which yet to be realised. Hence, the utilization of natural sunlight having higher luminous efficacy (an ability to produce visible light) rather than simulated

sunlight (requires significant cost and large infrastructure) to drive the chemical reactions to produce high value fine chemicals is the "holy grail" in the present scenario, where the environmental policies are becoming more stringent day-by-day.

Recently, visible light induced photoredox catalysis using inorganic transition metal complexes [4] and organic dyes [5] as homogeneous photocatalyst has shown successful results in a variety of chemical transformations due to their commercial availability, excellent stability and Photoredox properties. However, their intrinsic drawbacks and post-reaction removal cost of homogeneous catalysts, etc are the huge obstacles for large scale commercial applications. Therefore, metal-free, heterogeneous, visible-light driven photocatalysts which are recoverable and reusable with high stability are most needed to address the aforementioned concerns that are facing the industrial challenges today.

In this respect, in spite of few reports from other organic polymers, Graphitic carbon nitride polymers, g-CN (commonly known as g-C<sub>3</sub>N<sub>4</sub>) provided the momentum in this regard and have been explored for a series of metal-free heterogeneous photocatalytic reactions.[6] Very recently, another class of heterogeneous photocatalysts, Conjugated Microporous Polymers (CMPs),[7] with permanent high porosity, photoactive structure, chemical tunability, high thermal stability and high flexibility are the centre of attraction to explore them as photocatalysts either in the presence or absence of co-catalysts, The scope of CMPs as a metal free photocatalysts is much wider, because their optoelectronic properties can be easily engineered at the molecular level with the help of rich organic chemistry tools.[8] Thus, the CMPs have emerged as an efficient and stable platform for heterogeneous visible light-promoted chemical transformations such as molecular oxygen activation,[9a] selective oxidation of organic sulphides,[9b] C-C bond formation,[9c] reductive dehalogenation reaction,[9d] oxidative hydroxylation of aryl-boronic

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acids, visible light-initiated free radical and cationic polymerization, light-induced hydrogen evolution[8e,9,7e] etc.[9] However, we have noticed that nearly all the reports addressing the photocatalytic application use artificial sources, which requires an expensive setup and high energy light source. To address these issues, we thrived to perform the photocatalytic reactions under natural sunlight in the effective sunshine hours which is a cost-effective way for possible large scale catalytic applications in future.

In this report, we have developed a novel Truxene (Tx) based conjugated microporous polymer (Tx-CMP) having high specific surface area (SSA) for better harvesting of sunlight and effective mass transfer during catalytic process. We reasoned the choice of molecular entity, a  $C_3$ symmetric, star-shaped strong electron donating  $\pi$ -conjugated polyarene, to build polymeric framework for photocatalyst since its extensive use in the optoelectronic devices as photosensitizers, [10] photoresists, [11] organic lasers, [12] sensors, [13] OLEDs, [14] OFETs, [15] and OPVs.[16] Truxene is a fused trimer of fluorene molecule, where fluorene is already employed as a building block for the CMPs to drive various photocatalytic chemical transformation.[9a, 9d, 9e] With a strong motive that the introduction of Tx molecule in CMP will provide unique photocatalytic properties, we employed Tx-CMP as a metal-free sunlight active heterogeneous photocatalyst for the fundamental organic transformation of amines to corresponding imines. The imines also called Schiff bases are well known for their versatility as intermediates in the synthesis of pharmaceutical or biological active compounds and fine chemicals. [17] As per the available literature and to our best knowledge this is the first report, where we achieved >99 % conversion with 90% yield for oxidative homocoupling of benzylamine in natural sunlight by using a heterogeneous metal free organic photocatalyst within

4 h of reaction time. This, we believe as a major step forward in the field of organophotocatalysis.

#### **Results and Discussions**

In Scheme 1, the synthetic pathway of the conjugated porous polymer Tx-CMP is displayed in which Tx, a well-known electron donor, is attached as a 3D centre with phenyl units via palladium-catalysed Suzuki cross-coupling reaction to give the microporous polymer (Tx-CMP). More detailed synthesis of the monomer is provided in Scheme S1, see supporting information (SI). For comparison purpose, mesoporous carbon nitride (SG-CN) was synthesized according to the previous reported procedure.[6i] Titanium dioxide, TiO<sub>2</sub> (commercial P25) was used as such for comparing the photocatalytic activity with Tx-CMP and SG-CN.



**Scheme 1.** Synthesis route and idealized structure of Tx-CMP; Reaction conditions: (a) Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, DMF/H<sub>2</sub>O.

# **Characterization of catalyst**

Solid-state <sup>13</sup>C CP/MAS NMR spectrum showed signals at 23 and 46 ppm, which are assigned to the methyl groups and tertiary carbon of Tx units, respectively. The signals between 110 and 160 ppm can be assigned to the aromatic carbons in the polymer backbone (Figure S1, see SI). Thermogravimetric analysis (TGA) measurements showed that the conjugated network remained

intact up to ~400 °C (Figure S2, see SI). The successful establishment of porous framework of Tx-CMP is clearly verified by the N<sub>2</sub>-physisorption analysis (Figure 1a). The Type-I N<sub>2</sub>physisorption isotherms at 77 K displayed a steep nitrogen gas uptake at low relative pressure  $(p/p_0)$  below 0.1) reflecting the presence of micropores, with hysteresis loop indicating the presence of mesoporosity. The BET specific surface area was found as  $1022 \text{ m}^2/\text{g}$  with average pore volume 0.7 ccg<sup>-1</sup>. The pore diameter and distribution were obtained by DFT method as shown in the inset of Figure 1a showing a major proportion of micropores with dimensions ranging from 0.7-1.8 nm and also the evidence of mesoporosity. The diffuse reflectance UV-Vis (DRUV-Vis) spectrum (Figure 1b) of Tx-CMP showed a broad absorption band with the absorbance starting around 600 nm with a wide shoulder and the maximum absorbance peak centred around 400 nm. It showed the broad absorption range of the Tx-CMP polymers in the visible and UV light regions which is crucial for their activity in the natural sunlight. The characteristic broad shoulder in the spectrum of microporous polymer could partially be due to the light scattering effect originated from the broad pore size range in these porous polymers.[9d] The inset of Figure 1b showed the band gap of 2.6 eV calculated from the Tauc plot. The scanning electron microscope (SEM) images of Tx-CMP showed agglomerated flake type structures (Figure 1c and Figure S3, see SI). The elemental composition of Tx-CMP was estimated by X-ray photoelectron spectroscopy (XPS) as shown in Figure S4 indicating carbon is the majority component presents besides trace amount of oxygen and bromine at the dangling ends of the polymer. The conduction band minimum (CBM) was calculated as -0.4 V via Mott-Schottky electrochemical measurements (Figure S5, see SI). Based on CBM and optical band gap (2.6 eV), the valence band maximum (VBM) was estimated as 2.2 V (vs Ag/AgCl). It had been established that the generation of reactive oxygen species (ROS) and



**Figure 1.** a)  $N_2$ -physisorption isotherms and pore size distribution curve (inset). b) DRUV-Vis spectra and Tauc plot to calculate the optical band gap (inset). c) Scanning Electron Microscope image of Tx-CMP and d) Band energy diagram of TiO<sub>2</sub>, SG-CN and Tx-CMP.

the oxidation ability of holes depend on the valence band and conduction band positions of the semiconductors. As shown in Figure 1d, the VBM position is far positive (+2.4 V vs NHE) which indicates that the Tx-CMP is a better oxidant comparable to carbon nitride (+1.4 V). On the other hand, specific surface area (SSA) of a photocatalyst also can play an active role in the

photocatalytic activity. The SSA and pore volume of the employed photocatalysts, TiO<sub>2</sub> (P25) and SG-CN and Tx-CMP had been tabulated in Table S1 (see SI).

# Photocatalytic activity of catalyst in natural sunlight

Due to its high SSA, small optical band gap (2.6 eV) and appropriate band positions, we decided to explore Tx-CMP's photocatalytic activity for photo-oxidation of amines in the natural sunlight. Oxidative homocoupling of amines to corresponding imines were carried out by using oxygen as an oxidant and acetonitrile as solvent in the presence of sunlight as shown in Figure 2.



**Figure 2.** The photocatalytic reaction setup for the oxidative homocoupling of amines (Inset showing closer view of the round bottomed flask kept in sunlight to carryout oxidative homocoupling reactions). This photo was taken by one of the authors only.

The sunlight is largely available, inexpensive and inexhaustible source of energy which contains approximately 3% of UV, 44% of visible and 53% of NIR. This inspired us to explore the utilization of natural sunlight to drive the chemical reactions rather than other artificial sources of light which requires a lot of expenditure when possible large scale applications are concerned. Initially, the natural sunlight-driven oxidative homocoupling of benzylamine (BAN) was taken as model reaction with Tx-CMP, as a metal-free photocatalyst and the optimization conditions had been shown in Table 1. From entries 1-3, it is clear that the photocatalyst and sunlight are indispensable for this reaction. In presence of sunlight (average temp. =35.2 °C, solar intensity = 80.2 mW/cm<sup>2</sup>), >99% conversion was obtained with 90% yield within 4 h of reaction time (Table 1, entry 4). In order to study the individual effect of UV and Visible light portion of natural sunlight on the catalytic activity, we carried out a reaction with the simulated sunlight under full-arc conditions (T =35°C) and under visible light (>420 nm, T=35°C) by using 450 W Xe lamp operated at 400 W (Height was adjusted to give the intensity of 80 mW/cm<sup>2</sup>) separately which gave 88% and 75% yields respectively (Table 1, entries 5 and 6). The reason for the better yield in full-arc over visible light conditions could be attributed to its absorption in UV region. The reaction under open-air gave 79 % yield only (Table 1, entry 7). Moreover, these results also suggested that the Tx-CMP is an efficient natural sunlight active photocatalyst for the oxidative homocoupling of BANs to corresponding imine. The screen shot of GC-MS chromatogram of reaction mixture at 0 h, after 4 h in dark and sunlight, respectively were provided in Figure S6, see SI. The average temperature and average solar intensity during these whole studies in natural sunlight had been given in Table S2.

**Table1.** Optimization of the conditions for natural sunlight driven oxidative homocoupling of benzylamine.<sup>a</sup>

Entry	Catalyst	Amine	Product	TOF <sup>c</sup>
		conversion	selectivity/	
		(%) <sup>b</sup>	yield (%) <sup>b</sup>	
1	No Catalyst	0	-	-
2	No Catalyst, No light	0	-	-
3	Tx-CMP <sup>d</sup>	<1	100/-	-
4	Tx-CMP	>99	91/90	12.4
5	Tx-CMP <sup>e</sup>	>99	89/88	12.4
6	Tx-CMP <sup>f</sup>	77	97/75	9.6
7	Tx-CMP <sup>g</sup>	>99	80/79	12.4

<sup>a</sup>Reaction Conditions: BAN (0.5 mmol), Tx-CMP = 10 mg, Solvent = 5 mL Acetonitrile, Reaction time = 4 h in O<sub>2</sub> atmosphere, under natural sunlight. <sup>b</sup>Calculated by GC-MS. <sup>c</sup>TOF= mmol of benzylamine converted per gram of catalyst per h. <sup>d</sup>Without light. <sup>e</sup>Full-arc experiments(T=35 °C). <sup>f</sup>Under visible light (>420 nm, T=35 °C). <sup>g</sup>Under open air.

Further the catalytic activity of Tx-CMP was compared with commercially available TiO<sub>2</sub> (P25) and mesoporous carbon nitride (prepared by sol-gel route) SG-CN (characterized by several techniques, Figure S7 in the SI), for the photooxidation of BAN under natural sunlight. The catalytic activity of these catalysts in sunlight was found to be in the order: Tx-CMP > TiO<sub>2</sub> (P25) > SG-CN, which could be explained on the basis of their band position and surface area parameters as briefed above (Figure 3a). The better catalytic activity of TiO<sub>2</sub> (P25) over SG-CN

is due to its more positive valence band position and formation of surface complex with BAN which acts as an antenna for visible light absorption. [18] Even though, the valence band position of  $TiO_2(P25)$  is slight positive than that of Tx-CMP (Figure 1d), the catalytic performance of Tx-CMP is far superior to  $TiO_2(P25)$  essentially due to its high SSA and smaller band gap. Energy-dispersive X-ray spectroscopy (EDX) experiments showed the absence of any traces of Palladium present in the as-prepared Tx-CMP sample after the Suzuki-coupling reaction (Figure S8 in the SI) which ruled out the possibility of catalytic activity by palladium. From the above experiments, it could be inferred that the SSA and band position stimulated the superior photocatalytic activity of Tx-CMP as compared to  $TiO_2(P25)$  and SG-CN in direct sunlight.

### **Recyclability of catalyst**

To study the durability of Tx-CMP in natural sunlight, recyclability tests were conducted for five subsequent cycles. Before using the catalyst for next cycle, the catalyst was recovered by



Figure 3. a) Comparison bar diagram of Tx-CMP photocatalytic activity with  $TiO_2$  and SG-CN for oxidative homocoupling of benzylamine. b) Recyclability test of Tx-CMP in oxidative homocoupling of benzylamine. Reaction Conditions: Substrate (0.5 mmol), Tx-CMP = 10 mg, Solvent= 5 mL ACS Paragon Plus Environment

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centrifugation, washed with acetonitrile and dried at 120 °C in vacuum oven for overnight. As shown in Figure 3b, the conversion of BAN was >99% in each cycle with more than 90 % yield. Thus, the photocatalytic activity of Tx-CMP remained similar throughout its use in all cycles. We carried out the Solid-state <sup>13</sup>C CP/MAS NMR, FT-IR, DRUV-Vis, TGA and SEM analysis of recovered Tx-CMP after 5<sup>th</sup> cycle (Figure S9-S14, see SI). The result shows that Tx-CMP retained the similar structural features after being used for 5 consecutive cycles of reaction course. The SSA of Tx-CMP catalyst after 5<sup>th</sup> cycle was measured to be 904 m<sup>2</sup>/g (Figure S14, see SI). Only a minor loss in the surface area compared to that of the fresh one and the retention of the porous structure was observed. This indicated the superior performance and robustness of Tx-CMP as a metal-free photocatalyst for natural sunlight driven oxidative homocoupling of amines.

## **Mechanistic studies**

Based on the observation from the above experimental studies and previous reports, a plausible mechanistic pathway for the natural sunlight-driven oxidative homocoupling of amines (BAN has been taken as model) was proposed (Scheme 2). Generally, this reaction was initiated by the charge carriers, holes and electrons that were generated upon light absorption by Tx-CMP. The similar reaction when carried out under  $N_2$  atmosphere gave only 7% conversion of BAN to imine (Table 2, entry 1) which confirmed that the molecular  $O_2$  is essential for this reaction.

As reported previously, the molecular oxygen  $(O_2)$  is converted into reactive oxygen species (ROS) by electron or energy transfer process (superoxide radical  $(O_2^{-})$  and singlet oxygen  $(^1O_2)$ ) species.[8a, 8b] The holes in the valence band of Tx-CMP oxidized the BAN to benzylamine radical cation.[6g] On the formation of benzylamine radical cation the acidity of benzylic C-H



**Scheme 2.** Proposed mechanism for the natural sunlight driven oxidative homocoupling of benzylamine catalyzed by Tx-CMP.

(benzylic hydrogen) adjacent to amine functional group would increase. The formed ROS would further abstract the benzylic hydrogen from the benzylamine radical cation to form benzyliminium ion. To investigate the influence of benzylamine radical cation, the hole scavenger KI was added and found that the conversion of BAN was decreased drastically to 10% in presence of KI (Table 2, entry 2), which confirmed that the formation of benzylamine radical cation formation step is crucial for this reaction.

To shed more light on mechanistic pathways, the role of ROS in this sunlight driven oxidative homocoupling of BAN was investigated. When *p*-benzoquinone (BQ), a superoxide radical scavenger was added to the reaction mixture, the homocoupling of BAN decreased drastically to 30% in (Table 2, entry 3) which indicated the vital role of superoxide radicals.[19] The singlet oxygen scavenger sodium azide (NaN<sub>3</sub>) was also added to the reaction mixture and it was observed that the homocoupling of BAN decreased to 77% (Table 2, entry 4) which proved the role of singlet oxygen in this reaction pathway.[8b] To note that, the benzyliminium ion further

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converted into benzylimine with the formation of  $H_2O_2$  as side product. [20] The  $H_2O_2$  further dissociated into OH by the UV light present in the sunlight and might played a supportive role in the oxidation of BAN to corresponding imine. The formation of H<sub>2</sub>O<sub>2</sub> and its dissociation into OH radicals by UV light present in natural sunlight during the reaction has been proved by a controlled experiment by using of N.N-diethyl-1,4-phenylenediamine (DPD) (Figure S 15 in SI). Further, the benzylimine (detected in GC-MS at 5.3 min retention time (Figure S6 in the SI)) could react in 3 different ways: 1) Undergo dehydrogenative step to give benzonitrile (detected in GC-MS at 4.6 min retention time) [21]; 2) Converts into benzaldehyde (detected in GC-MS at 4.4 min retention time). This further could react with BAN to give corresponding imine. The formation of benzylimine was confirmed by the fragmentation spectra (Figure S16 in SI) and 3) Reacts with BAN to give corresponding imine.[8d, 22] In order to prove the formation of above intermediates, we monitored the reaction for initial 2 h. We observed that the concentration of benzaldehyde and benzonitrile increased for this time period (Figure S17 in the SI) with consequent decrease in concentration of reactant. The corresponding increase in the concentration of both (benzaldehyde and benzonitrile) indicated the formation of benzylimine intermediate which could undergo dehydrogenation and hydrolysis, respectively to benzonitrile and benzaldehyde. These additional experiments to understand the mechanism in the natural sunlight as observed earlier in high energy light sources prove the similar mechanistic pathway in the current study.

Table 2. Controlled experiments to predict the mechanism.<sup>a</sup>

Entry	O <sub>2</sub>	Additive	Amine	
			Conversion (%)	
1 <sup>b</sup>	-	-	7	

2	+	Hole scavenger	10
3	+	Superoxide	30
		scavenger	
4	+	Singlet oxygen	77
		scavenger	

<sup>a</sup>Reaction Conditions: Substrate (0.5 mmol), Tx-CMP = 10 mg, Solvent = 5 mL Acetonitrile, Reaction time = 4 h under direct sunlight,  ${}^{b}N_{2}$  atmosphere, KI as hole scavenger, p-benzoquinone as superoxide scavenger and NaN<sub>3</sub> as singlet oxygen scavenger.

# Substrate scope of the catalyst

Further to explore the versatility of Tx-CMP catalyst, various substituted BANs (Table 3) were used under same reaction condition. When BAN is substituted with electron withdrawing substituents (-Cl & -F), we achieved 77% and 82% conversion with 95% and 92% selectivity, respectively within 4 h of reaction time (Table 3, entry 2 and 3). However, the BAN substituted with electron donating substituents (-CH<sub>3</sub> & -OCH<sub>3</sub>) achieved 96% and 97% conversion with 80% and 81% selectivity, respectively, within 4 h reaction time (Table 3, entry 4 and 5). In addition, the applicability of Tx-CMP for oxidative homocoupling of heterocyclic amine (furfurylamine) was explored resulting in the 98% conversion with 86% selectivity (Table 3, entry 6). But the reaction with aliphatic amines (Dodecylamine and n-butylamine) could not give corresponding imine under these experimental conditions (Table 3, entry 7 and 8). In this case, only fragmentation products were observed in GC-MS spectrum. This is due to the activation of multiple reactive centres by reactive oxygen species which results in unselective auto-oxidation of aliphatic amines.[22b] The above experimental results suggested that Tx-CMP is a highly promising photocatalyst which can promote oxidative homocoupling of substituted amines and heterocyclic amines to corresponding imines with high conversion and selectivity within 4 h in natural sunlight.

Entry	Substrate	Product	Conversion	TOF <sup>b</sup>
			/selectivity (%)	
1	NH <sub>2</sub>		>99/91	12.4
2	CI NH2		77/95	9.6
3	F NH2	F	82/92	10.3
4	NH <sub>2</sub>		97/80	12.1
5	MeO NH2	Meo	96/81	12.0
6	ONH <sub>2</sub>		98/86	12.3
7	NH <sub>2</sub>	N/N/	0/0	-
8	←10 NH2	+ + N + + 10	0/0	-

<sup>a</sup>Reaction Conditions: Substrate (0.5 mmol), Tx-CMP = 10 mg, Solvent = 5 mL Acetonitrile, Reaction time = 4 h in O<sub>2</sub> atmosphere under direct sunlight. <sup>b</sup>TOF= mmol of amine converted per gram of catalyst per h.

# Conclusion

In summary, we have successfully designed a novel Truxene based conjugated microporous polymer (Tx-CMP) linked through highly stable C-C bond for the first time. The novel Tx-CMP has high surface area, large pore volume, narrow band gap and extraordinary stability. It serves

as a metal-free photocatalyst for the oxidative homocoupling of amines with optimal conversion under natural sunlight within 4 h. This model reaction also describes an effective, greener and sustainable way to harvest natural sunlight effectively for the organic transformations. Tx-CMP has shown recyclability without any decline in its catalytic activity. We hope this work opens the door for the employment of various conjugated microporous polymers as metal-free heterogeneous photocatalysts for effective harvesting of natural sunlight to drive many organic transformations.

## Methods

All chemicals and solvents were of analytical grade and used without further purifcation.1indanone, 1,4-phenylenediboronic acid, potassium carbonate and  $Pd(PPh_3)_4$  were purchased from Sigma Aldrich (Bangalore, India). Thin-layer chromatography was performed on aluminium sheets pre-coated with silica gel (Merck, Kiesel gel 60, F254). Column chromatographic separations were performed on silica gel (60-120 mesh). Structural characterisations of the compounds were conducted by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR (Bruker Biospin, Switzerland, Avance-iii 400 spectrometer), Infrared spectroscopy (Perkin Elmer Spectrum AX3) and DRUV-Vis spectrophotometer (3000+). NMR spectra were recorded in deuterated chloroform (CDCl<sub>3</sub>) and deuterated dimethylsulfoxide (DMSO-d<sub>6</sub>) using tetramethylsilane as the internal standard. SEM images were recorded on a JEOL 7600F instrument. N<sub>2</sub>-physisorption isotherms were recorded on Autosorb iQ<sub>2</sub> instrument (Quantachrome) at 77 K. Before measurements, samples were degassed overnight under vacuum at 120 °C. The specific surface area was calculated by the BET Micropore assistant surface area calculations for Tx-CMP. Density functional theory (DFT) method was employed to estimate the pore size distribution for Tx-CMP and BJH method for SG-CN. The total pore volume was calculated from the amount of N<sub>2</sub> adsorbed at  $p/p_0$  0.9,

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assuming that adsorption on the external surface was negligible compared to that of the pores. The optical band gap of Tx-CMP was derived from Tauc plot. Mott–Schottky electrochemical measurements were carried to get the information about the conductionband potential. Catalyst ink was prepared by dispersing the catalyst in ethanol, IPA, nafion and then working electrode was prepared by drop casting catalyst ink on the glassy carbon electrode (GCE) and left to dry overnight. Electrochemical impedance spectra measurements were carried out by standard three electrode system using Platinum wire and Ag/AgCl (3M KCl) as counter and reference electrodes, respectively. The measurement was conducted in a buffer solution (pH= 7) in the potential range of -0.6 to 1V. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector, with Cu-K<sub>a</sub> radiation ( $\lambda = 0.15418$  nm,  $2\theta = 5-80^{\circ}$ ) source operating at 40 kV and 40 mA. Diffuse reflectance UV-Visible (DRUV-Vis) spectra were recorded on a Shimadzu UV-2550 spectrophotometer. The elemental composition of Tx-CMP was estimated by using the XPS with AES module (PHI 5000 Versa Probe II, FEI Inc.).

# General procedure for oxidative homocoupling of amines

The oxidative homocoupling of amines was performed in a home-made photocatalytic vessel under direct sunlight (Figure 2). In a typical reaction, 0.5 mmol of BAN was added to 5 mL of acetonitrile solvent and then 10 mg of Tx-CMP was added. The reaction mixture was kept for stirring under natural sunlight (In Mohali, India, during May, June and August, 2017) and the O<sub>2</sub> atmosphere (1 atm) was maintained during the reaction. The date-wise average temperature and average solar intensity data was given in (Table S2, Figure S18). The catalyst was separated by micro centrifuge after the reaction for further characterization. Then, the conversion, selectivity and yield of the reaction products were quantified by gas chromatography (GC-MS Shimadzu

GC-2014) equipped with an HP-5 capillary column using calibration curves. The same procedure has been followed for the catalysis using  $TiO_2$  and SG-CN for better comparison.

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# **Author Contributions**

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## Notes

Authors declare no competing financial interests.

# ASSOCIATED CONTENT

# **Supporting Information**

Synthesis details, IR, Solid-state <sup>13</sup>C{<sup>1</sup>H} CP/MAS NMR spectra, BET, BJH, SEM, XPS-survey scan, EDX, XRD, TGA, Mott-Schottky measurement, Textural properties, Average Temperature and Solar intensity and GC-MS screen shot images along with Sunlight intensity and Temperature Tables.

### ACKNOWLEDGMENT

We thank INST Mohali and IISER Mohali for financial support. Dr K. Kailasam thanks DST-Nano Mission NATDP funded Technology Project, File No. SR/NM/NT-06/2016 and DST-

SERB for the Early Career Research Award (ECR), File No. ECR/2016/001469. Dr S. K. Pal is grateful for the financial support of the INSA (bearing Sanction No. SP/YSP/124/2015/ 433) and CSIR (bearing Sanction No. 02(0311)/17/EMR-II). Dr Sunil Kumar would like to acknowledge DST (India) SERB fellowship under project No. PDF/2016/002227.

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