Heterogeneous & Homogeneous & Bio- & Nano-
CHEMCATCHEM
CATALYSIS

Accepted Article

Title: Palladium Nanoparticles Supported on Nitrogen-rich Containing Melamine-Based Microporous Covalent Triazine Polymers as Efficient Heterogeneous Catalyst for C-Se Coupling Reactions

Authors: Sadhasivam Velu, Balasaravanan Rajendiran, Chithiraikumar Chinnadurai, and Siva Ayyanar

To be cited as: *ChemCatChem* 10.1002/cctc.201800400

Link to VoR: http://dx.doi.org/10.1002/cctc.201800400

A Journal of ChemPubSoc Europe

WILEY-VCH www.chemcatchem.org

Palladium Nanoparticles Supported on Nitrogen-rich Containing Melamine-based Microporous Covalent Triazine Polymers as Efficient Heterogeneous Catalyst for C-Se Coupling Reactions

Mr. Velu Sadhasivam, Dr. Rajendiran Balasaravanan, Mr. Chinnadurai Chithiraikumar and Prof. Dr. Ayyanar Siva*

Supramolecular and Organometallic Chemistry Lab, Department of Inorganic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai-625021, Tamil Nadu, India.

E-mail: drasiva@gmail.com.

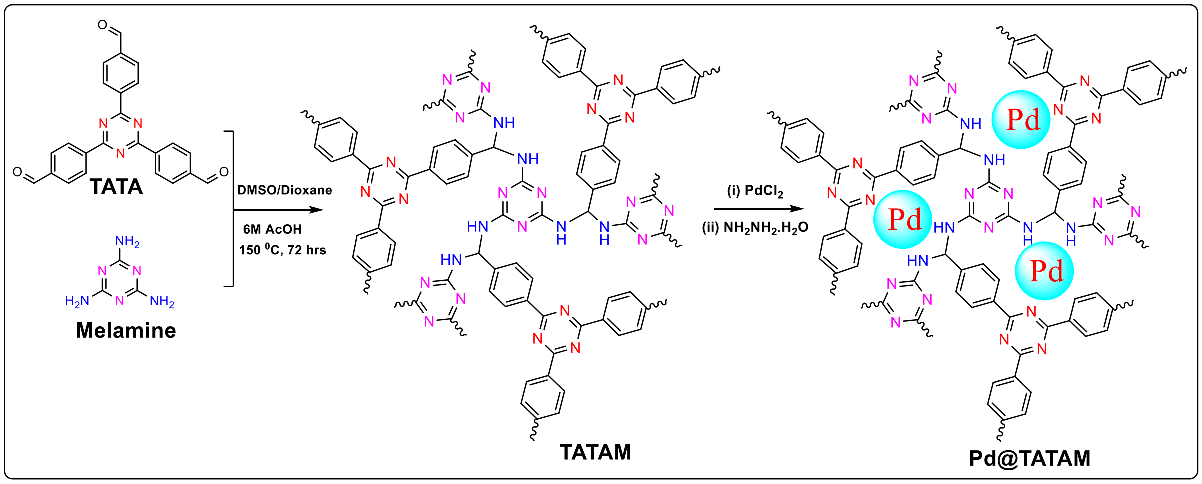
Abstract

In the present work, microporous nitrogen containing covalent triazine polymers (CTPs) TATAM was synthesized from condensation of 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)tribenzaldehyde (TATA) and melamine under solvothermal conditions to obtain nitrogen-rich triazine containing polymeric supported materials (TATAM). Further, palladium nanoparticles (Pd NPs) were supported on TATAM polymeric networks (Pd@TATAM). The synthesized Pd@TATAM CTPs material was thoroughly characterized by FT-IR, UV-DRS, solid state ^{13}C-CPMAS, XPS, powder X-ray diffraction, TGA, SEM, TEM. In addition, the characterized Pd@TATAM CTPs were applied to check the catalytic application. The Pd@TATAM showed to be an efficient and reusable heterogeneous solid catalyst for the formation of C-Se bond through coupling of aryl halide and elemental selenium, dimethylsulfoxide as a solvent at 100 °C for about 6 hrs. Besides the absence of metal leaching for catalytic system, it is also observed that the catalyst can be reused for three consecutive cycles with a minimal decrease in its activity.

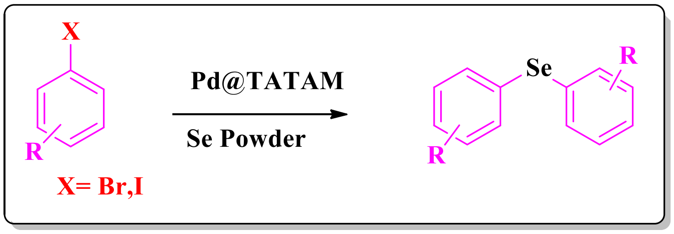
Introduction

Carbon and nitrogen-rich containing covalent organic frameworks (COFs) have grown into a major research field of material science, because of its remarkable potential applications such as photo catalyst, hydrogen storages, hydrogen production, gas storages,[1] membranes, electrodes, optoelectronic, gas separation, drug delivery, super hydrophobic interface and mainly used to heterogeneous catalysis.[2-9] The molecular building blocks of COFs materials are composed by light weight elements such as C, B, N, O linked by covalent bonds into a well-defined predictable two or three-dimensional (2D or 3D) porous crystalline networks.[10-15] These COFs materials are found to be efficient catalyst in organic synthesis due to their low density, high specific surface areas, large porosity and easy structural tunable functionality that can lead to efficient performances and selectivity of the organic reactions.[16] As some of the porous materials like COFs, porous silica and zeolites are used to supports incorporate metal nano particles (NPs) are unstable, metal leaching in aqueous and most organic solvents.[17] In order to overcome these issues, newly synthesized highly stable nitrogen containing porous materials in which there is a strong interaction between the metal support and the loaded materials (NPs).[18] Covalent triazine polymers (CTPs) are one of the nitrogen containing COFs, formed by the trimerization reaction of cyano-functionalized aromatic compounds to obtain triazine based linkages. CTPs have some remarkable properties due to their periodic columnar π-π stacking, ordered nano channels, high surface area and high amount of nitrogen atom present in the networks, which is beneficial to incorporate a large number of metal binding sites, namely, nitrogen on the surfaces of the supported materials to enhance the high catalytic activity as well as the stability of the supported materials.[19-21] Palkovits *et al.*, applied a CTPs loaded with a platinum metal as a catalyst for methane oxidation in concentrated sulfuric acid at harsh condition.[22] Recently, in our group also reported triazine based microporous covalent imine functionalized polymers as a novel solid supports for palladium mediated Suzuki-Miyaura coupling reaction.[23] In addition to that, CTPs supported catalyst showed no detectable degradation and change the structural integrity even after use to several reaction cycles.

In recent years, transition metal catalyzed cross coupling reactions such as C-C, C-N, C-O, C-Se bond formation reactions have achieved considerable progress in synthetic organic transformations, pharmaceutical and medicinal applications.[24] Over the decades, various homogeneous catalytic systems, which exhibit better activity and high selectivity have been developed for this transformations.[25] However, the homogeneous catalyst suffer from drawbacks such as expensive phosphine ligands, use of various additives, contamination of products, metal leaching, recyclability and tedious multistep protocol necessary for the ligand synthesis and to difficult work-up process and also phosphine ligands are very toxic in nature. In this manner, the heterogenization of the Pd catalyst has to overcome the above difficulties and make the process to green protocols. Recently, there has been an increasing demand for efficient methods to synthesize mono selenide and diselenides for organoselenium compounds, especially, these carbon-selenium bonds have been a fascinating topic for current research field, mainly these compounds are vital role in biological system for antioxidant, antimicrobial, antiviral for the pharmaceutical industry and material science applications.[26-28] Selenium is an one of the most important component for amino acids such as selenocysteine and selenomethionine, so the construction of C-Se bond formed by using various selenium sources, such as selenols,[29] diselenide,[30] $ArSeSnR_3$[31] under basic conditions.[32] Most of the aryl selenols suffer from trouble for handling, because of unpleasant odours, high sensitive to air and moisture, expensive and instability, which hamper their applications in pharmaceutical industry. In order to overcome the important shortcoming of organoselenium reagent, recently, the elemental selenium powder has been used as a selenating agent,[33] due to easy to handle, commercial available, stable material and low cost. Huayue Wu *et al*., reported aryl and heteroaryl selenation of indole using the elemental selenium as a selenating agent to obtain regioselective and high yield of product was observed.[34]



Scheme 1. Synthesis of Pd NPs supported on nitrogen rich covalent triazine polymer networks (Pd@TATAM).



Scheme 2. Synthesis of diarylmonoselenide from aryl halide for C-Se coupling reactions.

In this work, we have successfully synthesized nitrogen rich covalent triazine based CTPs may incorporate a large number of metal binding sites and robust stability. Herein, we report a novel strategy for the synthesis of palladium nanoparticles supported on nitrogen rich melamine-based microporous covalent triazine polymers as efficient heterogeneous catalyst for selenation of aryl halide (C-Se) coupling reactions and good catalytic activity with excellent yield under eco-friendly conditions. To the best of our knowledge, there are no reports describing the selenation of aryl halide using tiny amounts of Pd@TATAM CTPs (20 mg, 0.5 mol%) heterogeneous catalytic system for the clean synthesis of C-Se bond formations.

Results and Discussion

A new series of triazine based nitrogen containing TATAM and Pd@TATAM was synthesized under solvothermal conditions by condensation reaction between 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tribenzaldehyde (TATA) and melamine, DMSO/dioxane (1:2) solvent in the presence of glacial acetic acid at 150 °C for about 3 days to obtain nitrogen rich triazine supported materials (TATAM). After that, Pd NPs successfully incorporated into the TATAM polymeric materials (Pd@TATAM). The prepared CTPs materials were confirmed by FT-IR spectroscopy (Fig. 1). In this spectrum of raw materials, the core triazine ring C=N stretching and the primary amine group (NH_2 stretching) of melamine was appeared at 1520 and 3468 cm^{-1} respectively. Further, the carbonyl functional group of aldehyde C-H at 2830 cm^{-1} as well as (C=O stretching) at 1670 cm^{-1} (see SI Figure S1) was completely diminished in TATAM. It is suggested that the successfully conversion of starting material of melamine into TATAM through aminal linkage to form three-dimensional network polymers (see SI Figure S1)[35] compared with these materials (TATAM and Pd@TATAM) revealed that both are similar pattern observed and the Pd@TATAM does not show any changes for absorption position, it is clearly indicated that the structural regularity was well maintained after incorporating Pd NPs.

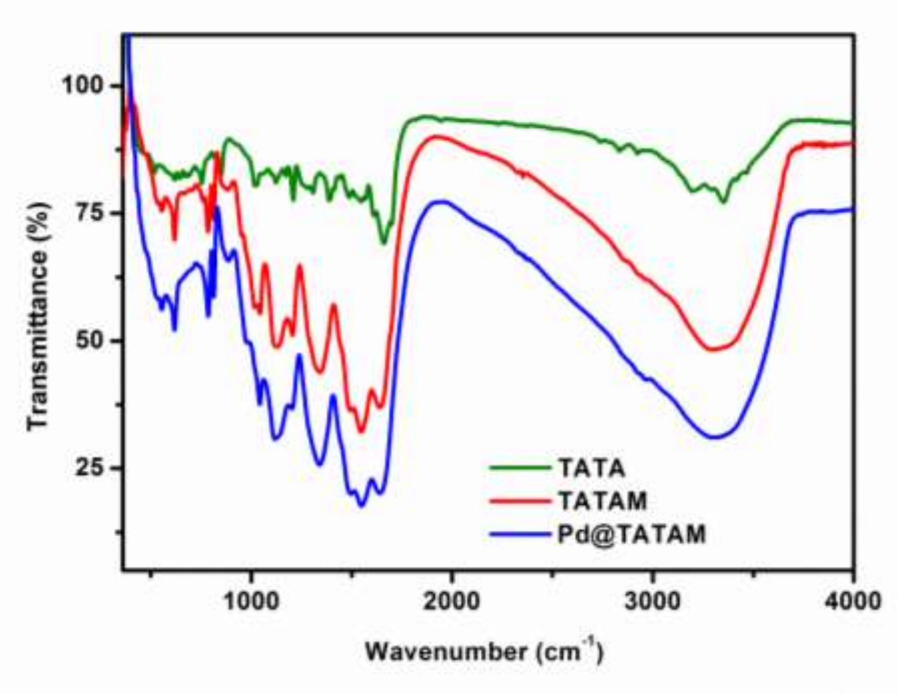


Figure 1. FT-IR Spectra of compounds TATA, TATAM and Pd@TATAM.

Solid state UV-Visible spectroscopy is an effective technique to investigate whether the metal precursors are completely reduced or not and the metal NPs are supported or not. The absorption spectra of both the TATAM and Pd@TATAM shows the two absorption band appeared at 217 nm and 250 nm, which may be attributed to π-π* and n-π* transition of C=C, C=N respectively, which are shown in Fig. 2. In addition to that, Pd@TATAM shows the new broad absorption band appeared at near 335 nm, which is due to the charge-transfer transitions of an electron excited from the triazine nitrogen lone pair to a vacant d-orbitals of the metallic nanoparticles.[36, 37] Thus the solid state UV-DRS clearly stipulate all the palladium precursor is completely reduced to Pd NPs, hence it is clearly revealed that all Pd NPs are successfully incorporated on nitrogen-rich containing TATAM networks.

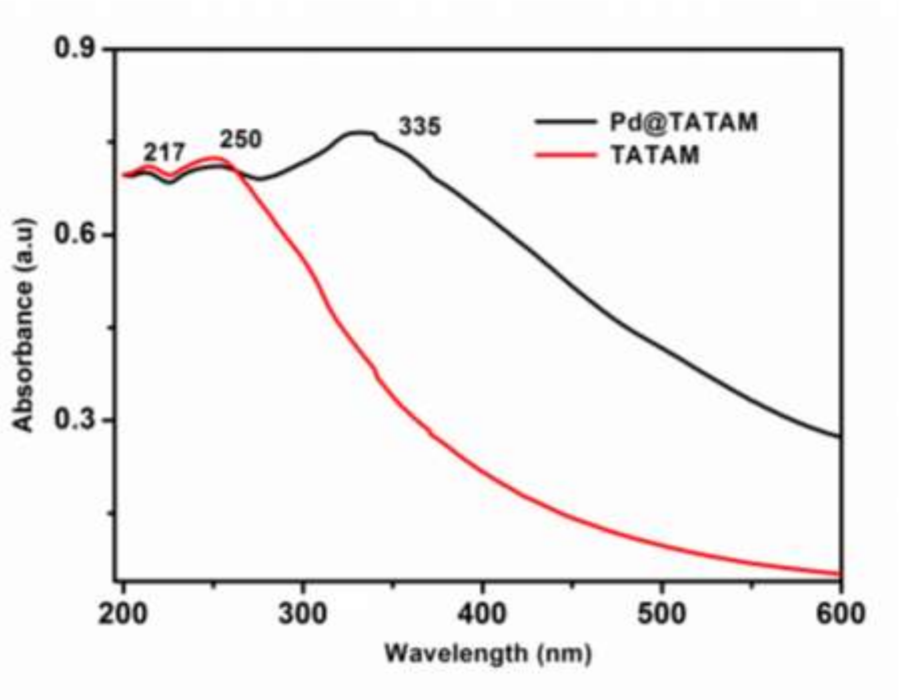


Figure 2. UV-DRS spectra of TATAM and Pd@TATAM.

The crystalline nature and structural regularity of both TATAM and Pd@TATAM were determined by powder XRD analysis which is shown in Fig. 3. The obtained powder XRD pattern TATAM shows partial crystallinity of the material, due to the range of 16 to 30^o 2θ values. This set of broad peaks suggests that TATAM material has a certain degree of order.[38] The comparison of TATAM and Pd@TATAM revealed that TATAM was well maintained after the synthesis of Pd@TATAM, because of these both materials have similar patterns was observed. It is also confirmed by FTIR spectrum, but the Pd@TATAM additionally new small peak was observed in these 2θ values at 12.62°, 40.07° and 46.13°, which are assigned to the refractions from the corresponding (100), (111) and (200) planes, indicating the face centered cubic (fcc) lattice for Pd NPs,[39] the broad diffraction peak at 12.62^o ascribed to Pd NPs strongly binding/interaction with triazine unit as well π-π stacking between aromatic ring and triazine unit to form certain degree of order, which is consistent with our reported literature.[23] These powder

XRD results clearly indicating the synthesized materials (Pd@TATAM) are partial crystalline in nature and Pd NPs high dispersion on TATAM network.

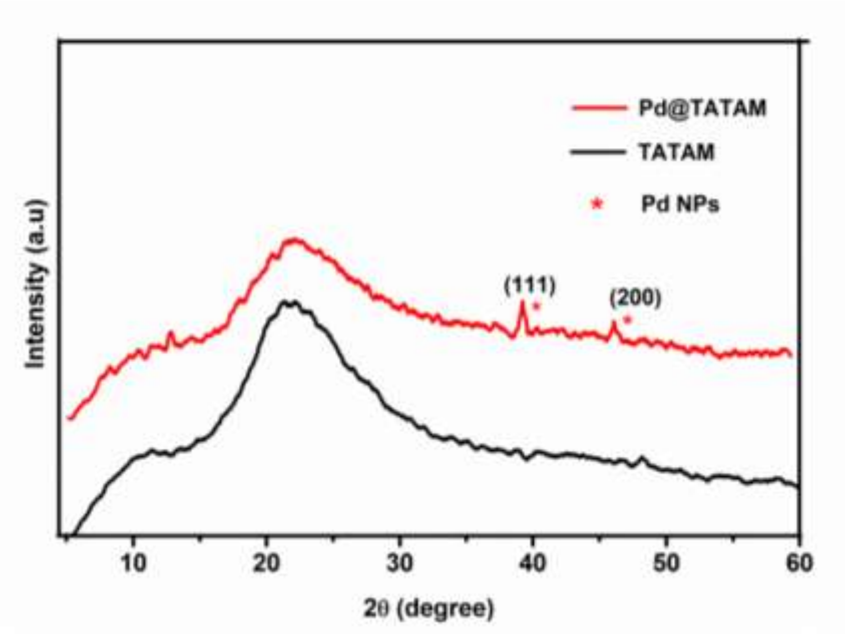


Figure 3. Powder XRD pattern of TATAM and Pd@TATAM.

The ^{13}C CP-MAS solid state NMR spectrum is further utilized to confirm the molecular structure of TATAM. As shown in Fig. 4, a five characteristic resonance signals at 167.93, 137.25, 126.66, 50.17, 13.09 ppm were observed. The signal at 167.93 corresponds to aromatic ring of core triazine carbon, whereas the signals appeared at 137.25 and 126.66 ppm originates from the aromatic C-H phenyl ring carbons. Furthermore, the carbonyl carbon at 190 ppm was greatly attenuated and the signal at 50.17 ppm corresponds to carbon attached to the aminal linked polymeric network was formed instead of imine linkage. The C=N characteristic resonance peak of imine bond at 160 ppm was not observed. Thus the ^{13}C CP-MAS solid state NMR spectrum clearly indicating melamine incorporated into TATAM polymeric network through an aminal linkage *via* the condensation of triazine aldehydes and primary amine of melamine. Which is consistent with the previous literature.[40, 41]

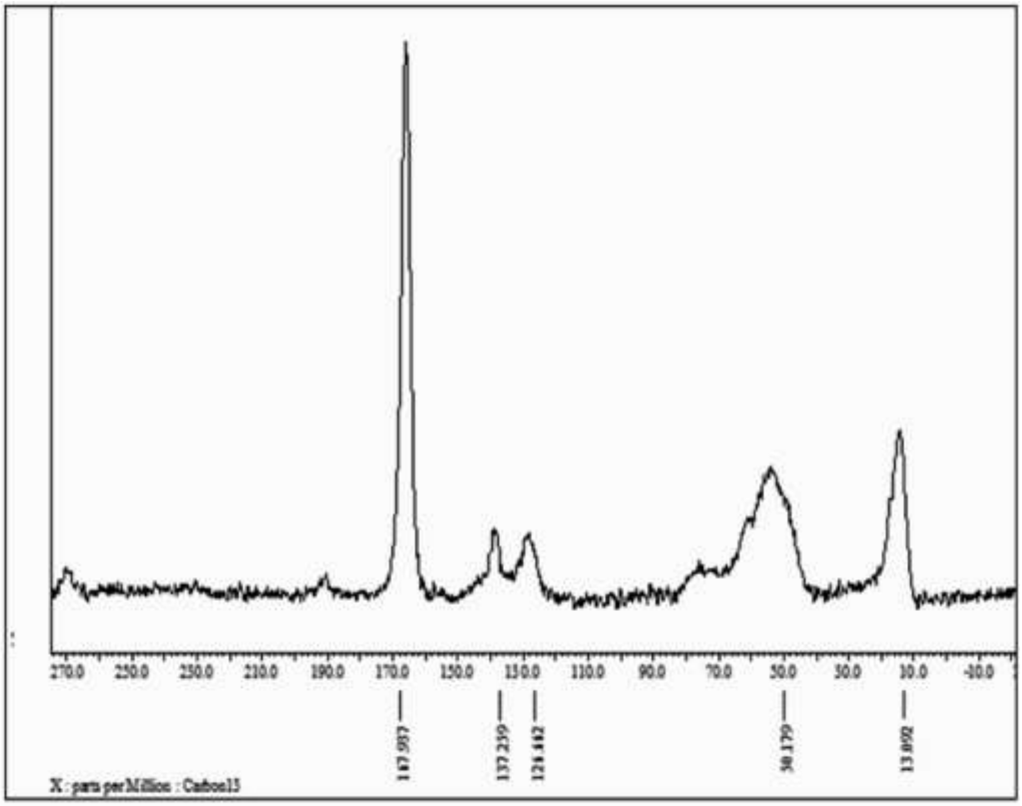


Figure 4.^{13}C-CP MAS NMR spectrum of TATAM.

The thermal stability of TATAM and Pd@TATAM were measured by thermo gravimetric analysis (TGA) under nitrogen atmosphere, the temperature up to 800 °C and heating flow rate is 5 °C/min shown in Fig. 5. From this figure, both materials have exhibits 4% of weight loss within a temperature near 135 °C, this is due to desorption takes place the physisorbed molecule loss of moisture and solvent molecules trapped inside the polymeric frame. Furthermore, the second weight loss of these materials takes place above 350 °C (and continuing to 365 °C) is related to the decomposition of the melamine linker from the Pd@TATAM covalent organic polymeric network. From the observed results, it is confirmed that the Pd@TATAM stable up to 365 °C. Pd@TATAM is also revealed that high thermal stability similar to that of TATAM materials.

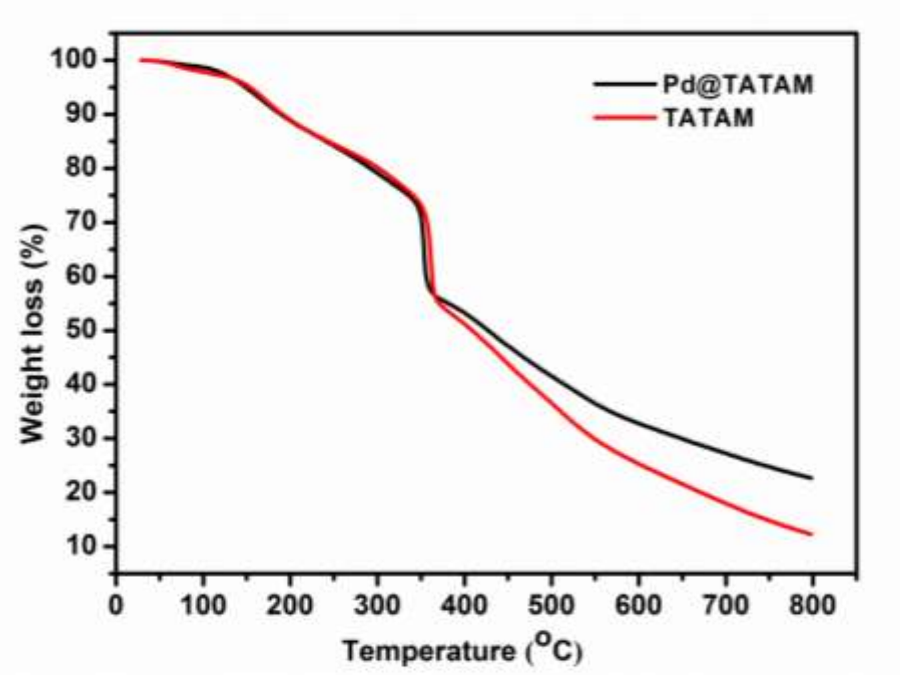


Figure 5. Thermogravimetric analysis of compounds TATAM and Pd@TATAM.

The surface area, pore volume and microporous nature of nitrogen-rich CTPs were further supported by the N_2 adsorption/desorption isotherm measurement at 77K (Fig. 6). The application of the Brunauer Emmett Teller (BET) resulted in the surface areas and pore volume of these material was found to be 213 m^2 g^{-1} and 0.5492cm^2g^{-1} (P/P_o= 0.985) respectively for Pd@TATAM. The pore size distribution of Pd@TATAM was calculated *via* NLDFT (nonlocal density functional theory) methods applied to the N_2 isotherms presented at (Fig. 6b) the pore size value 5.2 Å and it’s a microporous material.

10.1002/cctc.201800400

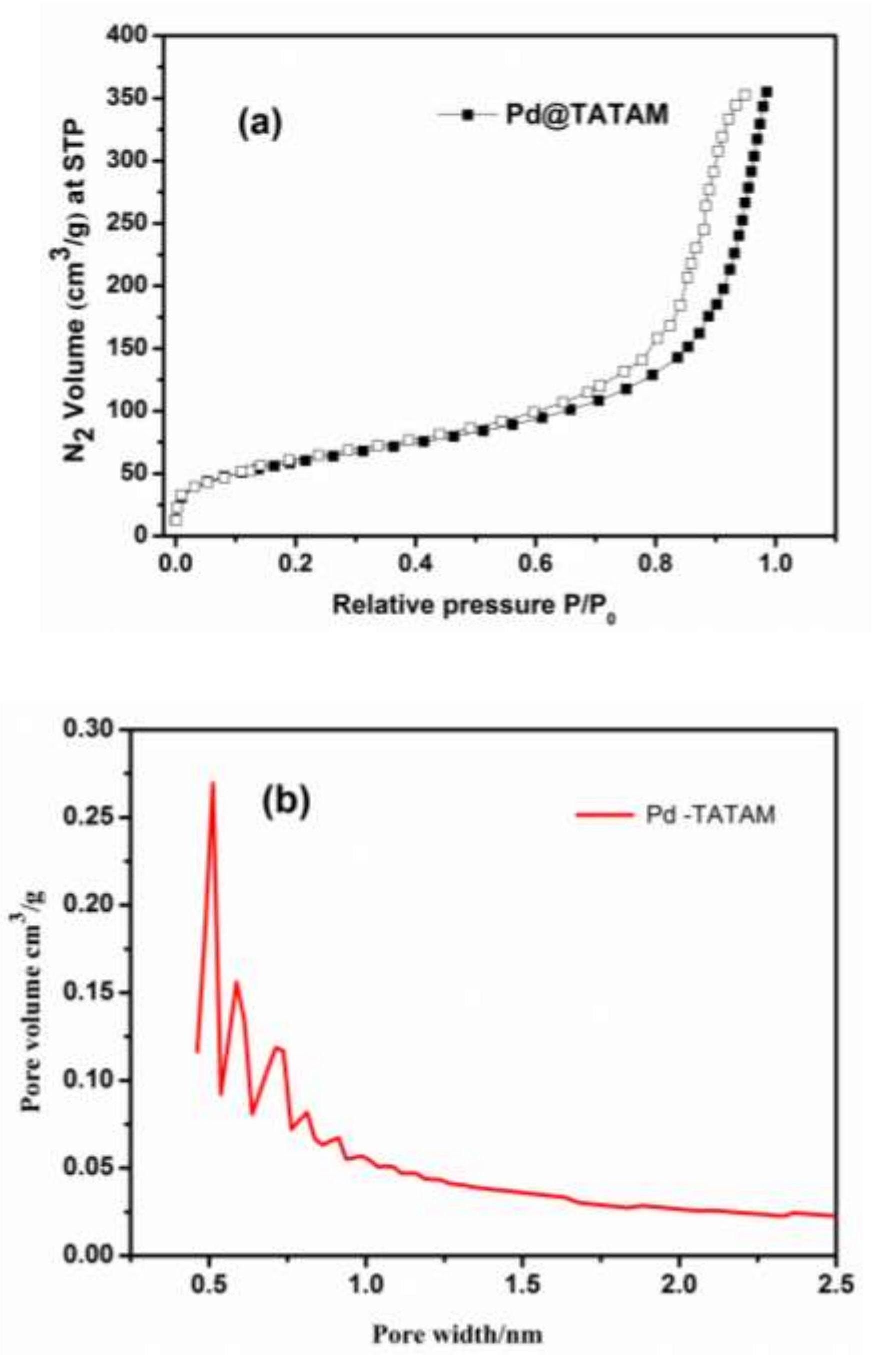
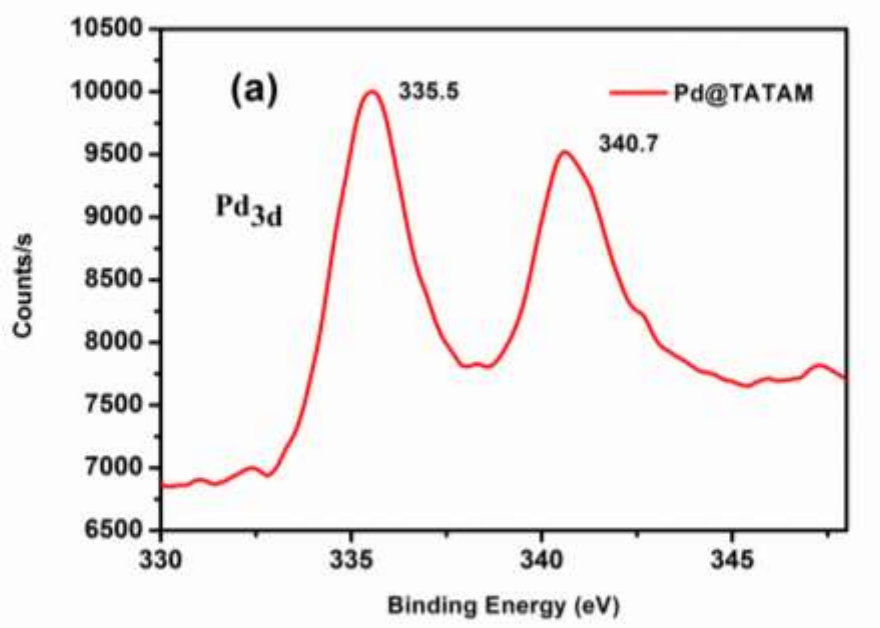


Figure 6. (a) N_2 adsorption (filled symbol) / desorption (empty symbol) and (b) pore size distribution of Pd@TATAM.

The oxidation state and binding affinity of Pd NPs in the Pd@TATAM catalyst was confirmed by the XPS spectrum as shown in the Fig. 7. The two binding energy peaks appeared at 335.5 eV and 340.7 eV corresponds to $Pd_{3d5/2}$ and $Pd_{3d3/2}$ core level respectively and these values are matched with some reported literature (Fig. 7a),[42,43] which clearly indicating that the Pd@TATAM catalyst was incorporated by palladium species and all are presented in metallic state of Pd(0). In addition to that, there is an another component peak at 285.22 eV corresponding to the C1s in the C=N bonds for triazine is observed and one additional small peak at 288.19 eV is appeared corresponds to sp^3 bond of C-N single bonds.[44,41] These results are clearly suggested that the aldehyde and amine are coupled with aminal linkages in TATAM covalent triazine network polymer and further survey scan of the Pd@TATAM material also support the palladium was bind with CTPs material as shown in Fig. 8g.



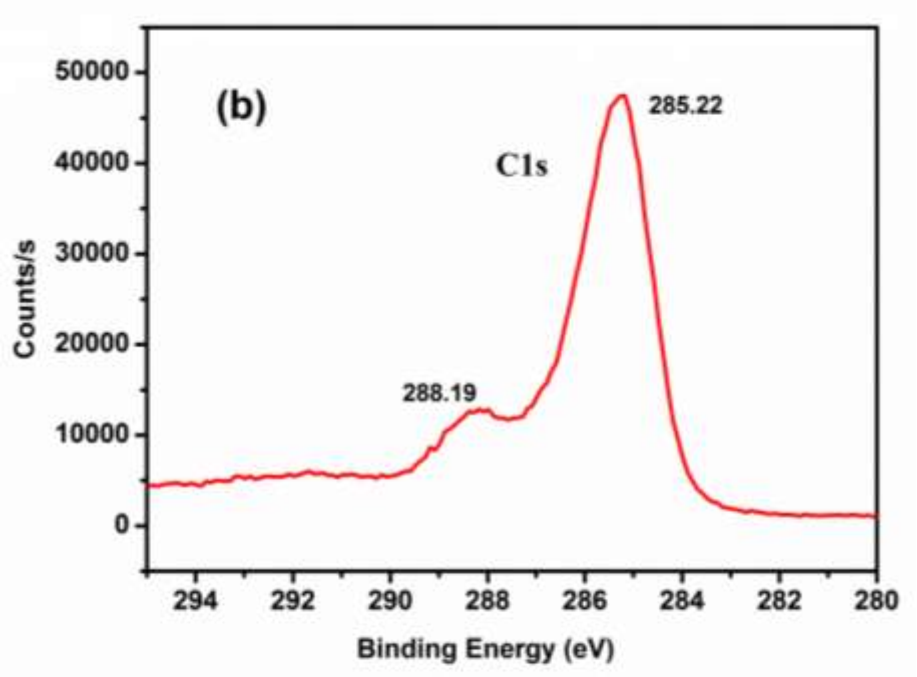


Figure 7. XPS analysis of (a) Pd_{3d} and (b) C_{1S} spectra for Pd@TATAM.

The structural morphology of TATAM and Pd@TATAM were confirmed by SEM and TEM analysis which are shown in Fig. 8. SEM images and elemental mapping of both materials showed direct visualization of porous cross-linked polymers with partially crystalline structures and distribution of Pd NPs. (see SI Figures S6, S7 and S8). In addition, transmission electron microscopy (TEM) analysis was further used to predict the dispersion of palladium nanoparticles in the Pd@TATAM catalyst. TEM images showed that Pd nanoparticles are dispersed (black dots) on TATAM, sponge cake like porous structure was observed (Fig. 8c-8f). Moreover, the average particle size of Pd@TATAM approximately 2.90 nm, and mean particle size of Pd/TATAE around 2.40 nm calculated from the XRD full width at half maximum (FWHM) using the Debye-Scherrer equation. Pd Nps are highly dispersed within the porous TATAM network (see SI Figure S9). Furthermore, the elemental composition of both materials was confirmed by EDS analysis (see SI Figures S3 & S4).

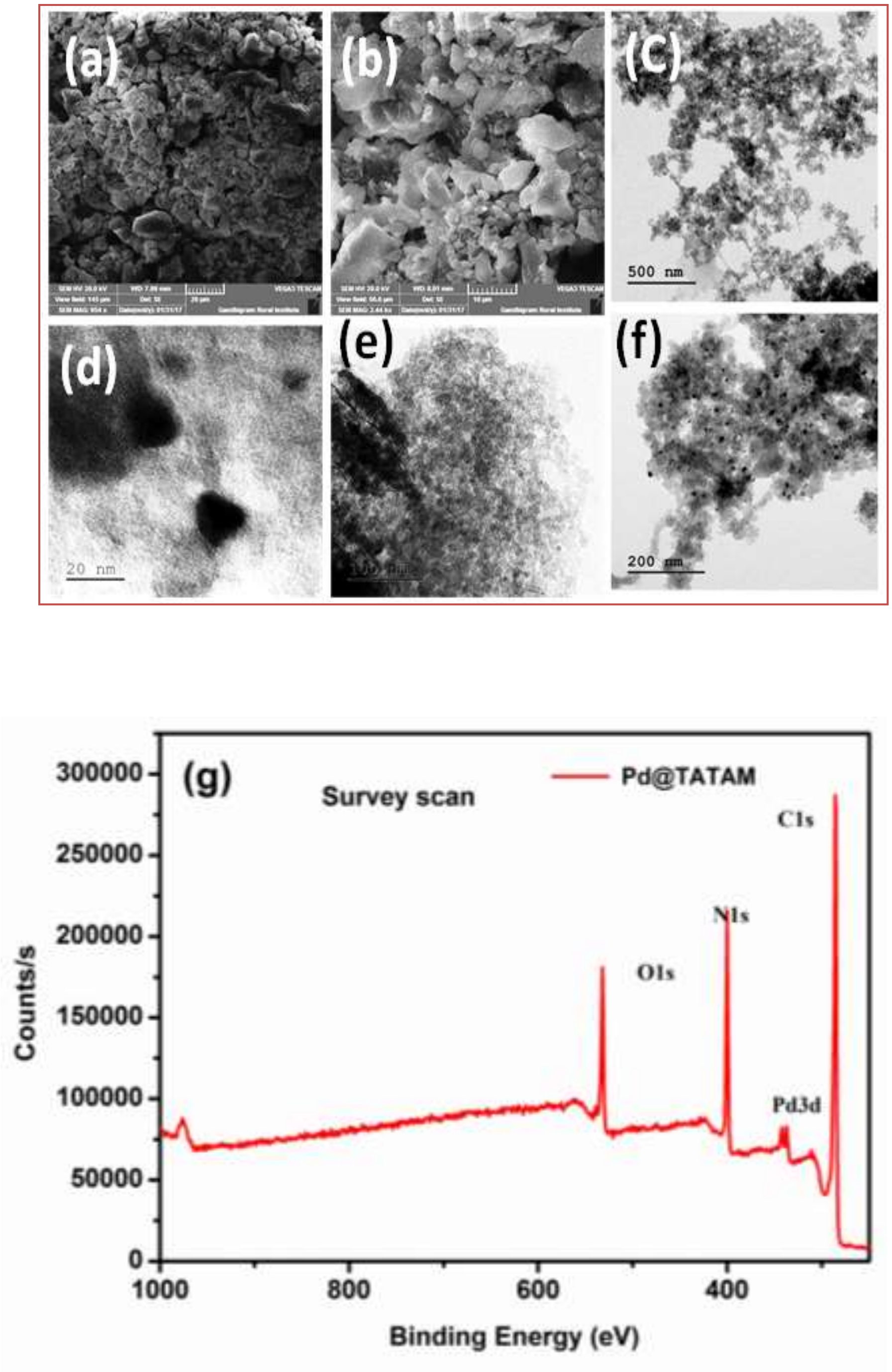


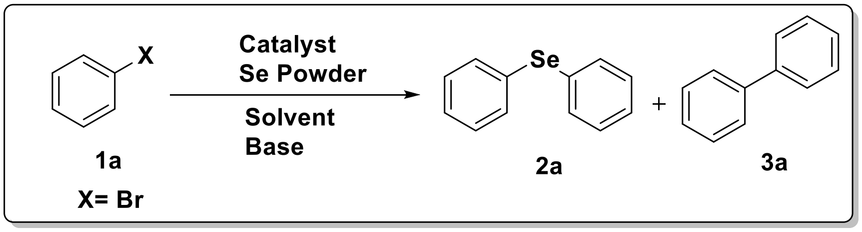
Figure 8. (a, b) SEM images of TATAM and Pd@TATAM, (c, d, e, f) TEM images of Pd@TATAM, (g) the overall survey scan of XPS analysis for Pd@TATAM.

Catalytic studies of Pd@TATAM in selenation of aryl halide for C-Se coupling reactions

In order to check the potential catalytic activity of Pd@TATAM material, we first optimize the reaction condition for monoselenation of aryl halide, starting from the reaction between aryl halide **1a** with elemental selenium in DMSO as a solvent and K_3PO_4 as a base in an air atmosphere at 100 °C to obtain diphenylmonoselenide (**2a**) as a major product and small amount of Ullmann homo coupled byproduct (**3a)** were obtained. Herein, bromobenzene and elemental selenium were chosen as model substrates to determine the optimal reaction conditions. The results are summarized in Table 1. Under controlled experimental condition the reaction was performed, no product was formed either in the presence of TATAM or absence of Pd incorporated catalyst (Table 1, entries 1, 2). Moreover, the reaction was performed without base (Table 1, entry 21) to obtain the less amount of yield (24%). This is confirmed that Pd NPs and base plays an important role in the catalytic reactions and further, the reaction was carried out in room temperature (Table 1, entry 20), we observed no product was obtained. Moreover, the elemental selenium does not activate in room temperature, so increase temperature up to 100 °C then only reaction was undergoes. Next optimization of the solvent condition, we chosen different polar/non polar solvents, such as DMF, DMSO, toluene, acetonitrile, dioxane and DMSO/H_2O mixture (Table 1, entries 3-8). Among the solvents DMSO gave an excellent amount of yield (84%) of the product observed at 100°C temperature (Table 1, entry 7). Other solvents like toluene, acetonitrile, and dioxane are provided trace amount of the products (Table 1, entries 3, 4 and 6). This may be due to the DMSO is more polar aprotic solvent that dissolve polar and non polar reactants and also the sulfur centre in DMSO is nucleophilic toward soft electrophiles and the oxygen is nucleophilic toward hard electrophiles with aryl/alkyl halide to form alkylated/arylatedsulfoxonium halide, which is more efficient intermediate in this selenium insertion reaction. In addition, various organic and inorganic bases were also studied like K_2CO_3, Cs_2CO_3, NEt_3, NaOH and K_3PO_4 (Table 1, entries 9-12). All bases gave a moderate amount of yield except K_3PO_4 which gave an excellent amount of yield 84% (Table 1, entries 13), due to the efficiency of the reaction was strongly dependent on their base strength, probably K_3PO_4 base was involved in the activation of the Se-Se bond of the elemental selenium (Se_8) and base K_3PO_4 was required to promote Se^{2-} anion with Pd@TATAM catalyst to activate the reaction.

Next, we further examine the various substrate scope, the elemental selenium with various substituted aryl halides (X = I, Br) were studied and the results are listed in Table 2, (entries 1-12). The reaction was conducted with a wide range of substrates containing both electron-withdrawing and donating groups substituted on bromobenzene gave diaryl substituted monoselenide products with excellent yield up to 84% and high turnover number upto1127 (Table 2, entry 1). The substituent's electron donating and electron withdrawing groups did not show any significant influence during the course of the reactions, which suggests that electronic character has no obvious effect on the catalytic system. In addition, the electronic properties of *ortho* and *meta* substituted aryl halide had little influence of yield (Table 2, entry 5), due to steric hindrance between the aryl halide and palladium catalyst, only less amount of substrate approaches to Pd@TATAM. Moreover, the synthesis of unsymmetrical diarylselenides to give less amount of yields (38%, 42%, 46%), because of symmetric diaryl selenides by-products also obtained during the course of these reactions (Table 2, entry 13,14,15).

Table 1. Optimization of Pd@TATAM-Catalyzed Mono-selenation of aryl halide with elemental Selenium [a]

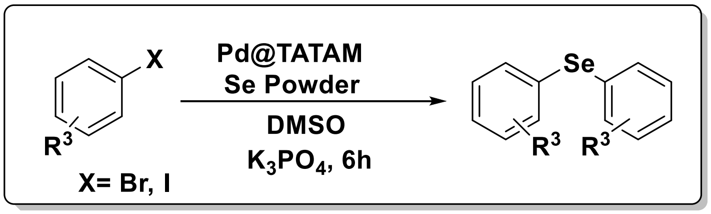


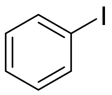
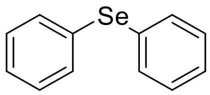
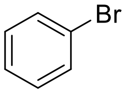
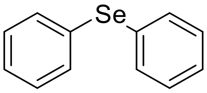
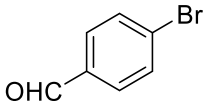
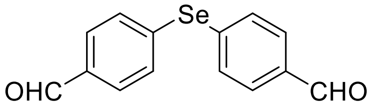
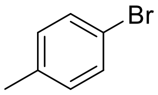
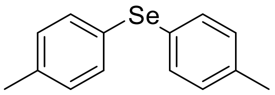
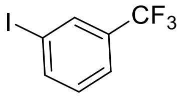
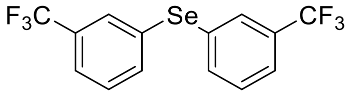
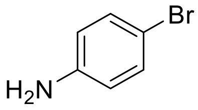
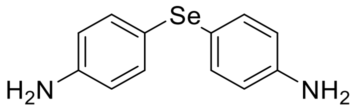
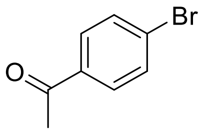
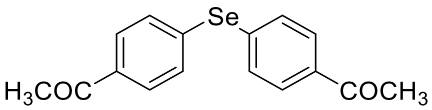
Entry	Catalyst	Solvent	Base	Temperature (°C)	Yield[b] 2a (%)	Yield[c] 3a (%)
1	TATAM	DMSO	K_3PO_4	100	NR[d]	NR[d]
2	-	DMSO	K_3PO_4	100	NR[d]	NR[d]
3	Pd@TATAM	Dioxane	K_3PO_4	100	21	11
4	Pd@TATAM	Toluene	K_3PO_4	100	-	5
5	Pd@TATAM	DMF	K_3PO_4	100	50	22
6	Pd@TATAM	ACN	K_3PO_4	75	-	trace
7	Pd@TATAM	DMSO	K_3PO_4	100	82	15
8	Pd@TATAM	DMSO-H_2O	K_3PO_4	100	-	10
9	Pd@TATAM	DMSO	K_2CO_3	100	29	trace
10	Pd@TATAM	DMSO	Cs_2CO_3	100	42	trace
11	Pd@TATAM	DMSO	NaOH	100	59	14
12	Pd@TATAM	DMSO	TEA	100	51	14
13	Pd@TATAM	DMSO	K_3PO_4	100	84	15
14[e]	Pd@TATAM	DMSO	K_3PO_4	100	50	15
15	$PdCl_2$	DMSO	K_3PO_4	100	5	8
16	Pd(OAC)$_2$	DMSO	K_3PO_4	100	24	trace
17	Pd@TATAM	DMSO	K_3PO_4	100	83	15

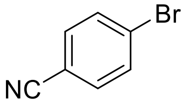
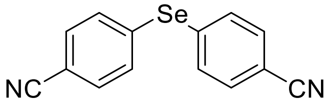
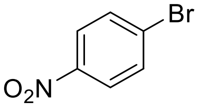
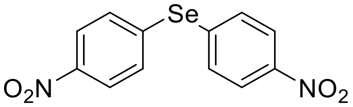
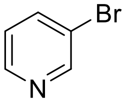
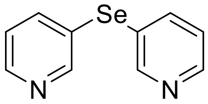
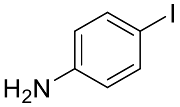
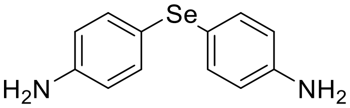
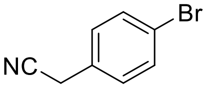
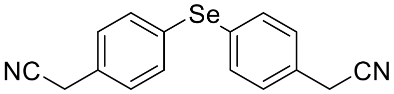
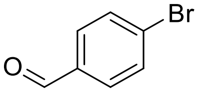
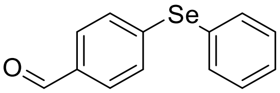
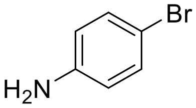
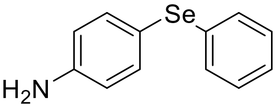
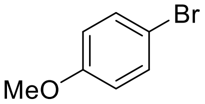
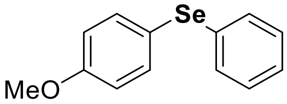
18	Pd@TATAM	DMSO	K_3PO_4	90	82	16
19	Pd@TATAM	DMSO	K_3PO_4	120	84	trace
20	Pd@TATAM	DMSO	K_3PO_4	RT	NR	NR
21	Pd@TATAM	DMSO	-	100	24	-

[a]Reaction condition: bromo benzene (1 mmol), elemental selenium (1 mmol), base (1.5 mmol), solvent (2 mL), catalyst (20 mg of Pd@TATAM thePd content 0.034 mg), 100°C, 6 h. [b] Isolated yield based on bromo benzene. [c] Small amount of biphenyl homo coupled product, [d] NR = no reaction, [e] 10 mg of Pd@TATAM.

Table 2. Pd@TATAM-catalyzed mono-selenation of various aryl halides[a] with elemental selenium.



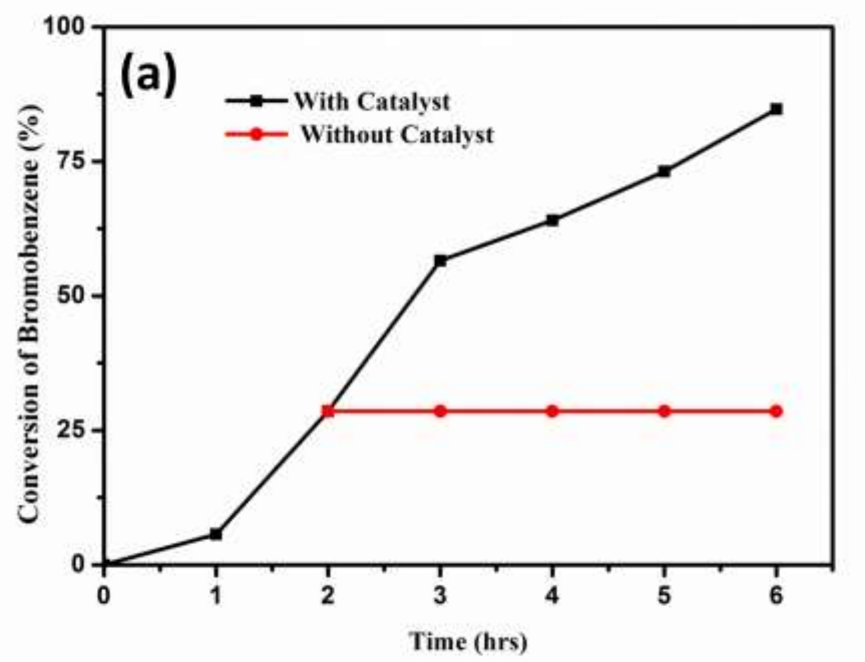
Entry	R-X	Product	code	Yield (%)	TON
1			2a	84	1127
2			2b	82	1115
3			2c	70	757
4			2d	76	910
5			2e	76	644
6			2f	78	927
7			2g	71	701

8			2h	72	795
9			2i	67	648
10			2j	62	825
11			2k	81	963
12			2l	75	895
13[b]			2m	38	368
14[b]			2n	42	406
15[b]			2o	46	438

[a] Aryl halides (1mmol), elemental selenium (1 mmol), K_3PO_4 (1.5 mmol), DMSO (2 mL), Pd@TATAM (20 mg, 0.034 mg of Pd content), 100°C, 6h, Isolated yield based on aryl bromide. [b] synthesis of unsymmetrical diaryl selenides from 4-substituted aryl halide (1mmol), bromobenzene (1 mmol), elemental selenium (1 mmol), K_3PO_4 (1.5 mmol).

Shelton test

In order to check the heterogeneity of Pd@TATAM catalyst in our system were analyzed by the Shelton test under the optimized reaction conditions. Shelton test was performed in selenation of bromobenzene with elemental selenium as a model substrate (Figure 9a). The solid catalyst Pd@TATAM was separated from the reaction mixture by simple centrifugation at this time 2 hrs (conversion 25.5%); then filtrate solution was performed for a further 4 h and the reaction mixture was analyzed by gas chromatographic technique, which showed no improvement in the product conversion. This result indicates that no leaching of Pd NPs in the filtrate solution and confirmed that the catalyst is truly heterogeneous in nature and Pd NPs are strongly supported in the TATAM network.



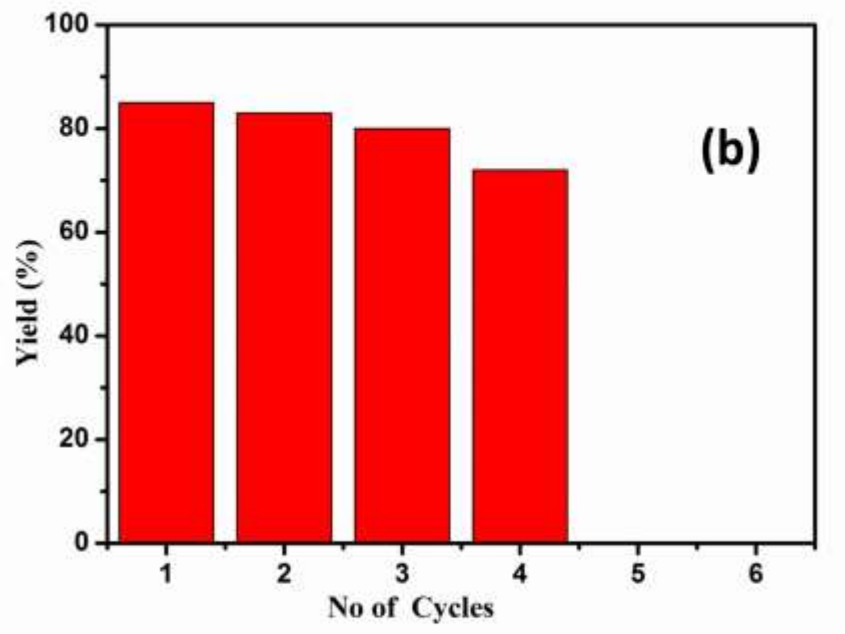
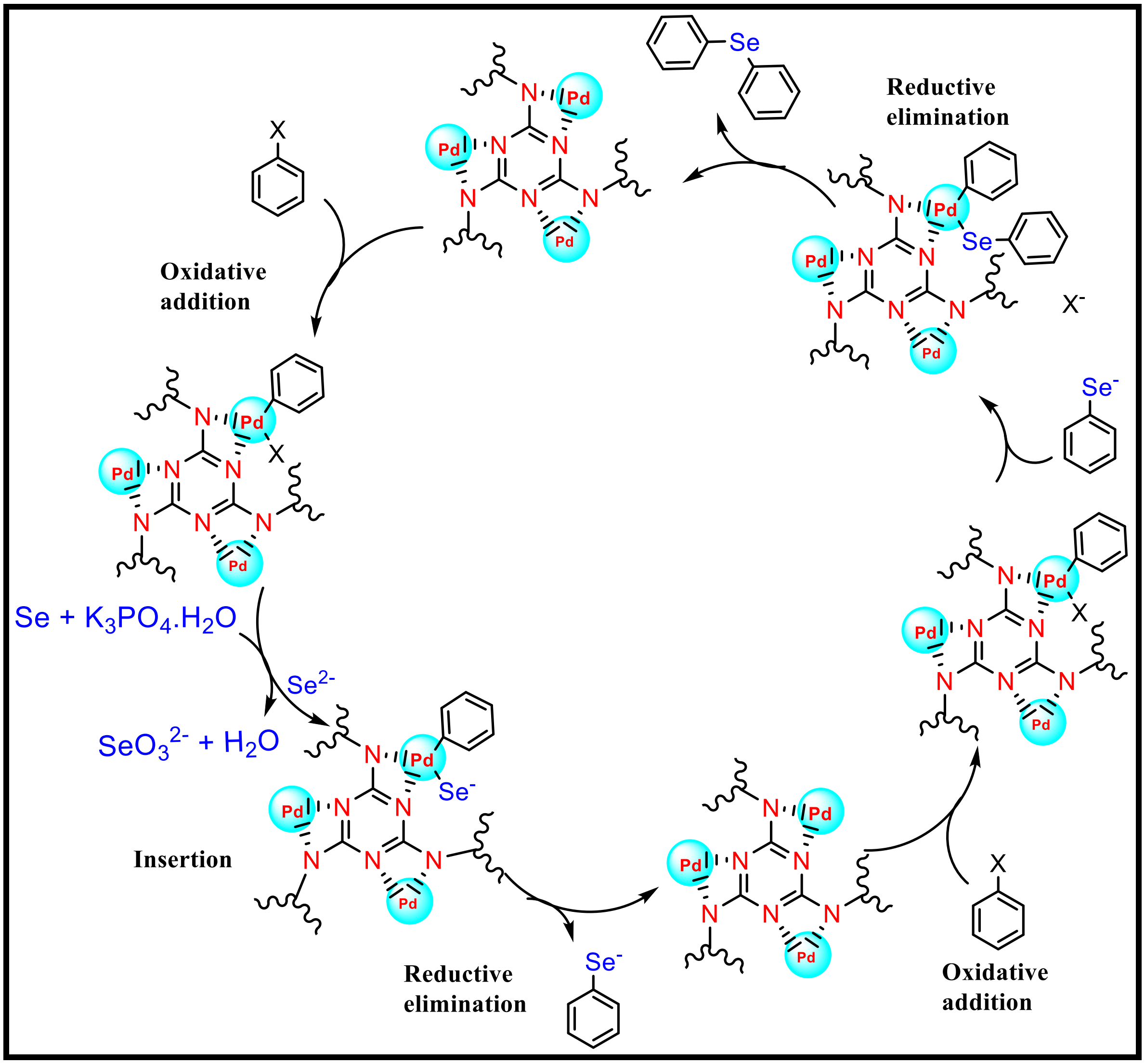


Figure 9. (a) Effect of reaction time and the percentage of bromo benzene conversion in Pd@TATAM catalyzed C-Se coupling reactions and Hot filtration test for Pd@TATAM catalyst, (b) Reusability experiment of Pd/TATAE catalyst.

Reusability test

Generally, the solid catalyst is one of the major important issues in metal supported heterogeneous catalysis while during the course of the reactions. Some of the metal supported catalysts are not reusable, unstable, tricky work up procedure and remarkable decreasing in catalyst efficiency. In our catalytic system the reusability test was performed in the mono selenation (C-Se) reaction and it was carried out with optimized reaction conditions to obtain 84% of yield. After that the catalyst was filtered and washed with water and to add the excess amount of acetone to remove the inorganic base, unreacted selenates and other impurities. Finally, the recovered catalyst was dried in a vacuum oven for 30 minutes. After the catalyst was reused for another three consecutive cycles under the same reaction conditions, no significant loss of catalytic activity (84%, 83%, 80% and 72% of yield) observed. On the basis of the above results, and also in accordance with previous literature reports,[45, 32] a plausible mechanism is proposed and shown in Scheme 4.



Scheme 4. Plausible mechanism for the Pd@TATAM catalyzed C-Se coupling reactions.

Table 5. Previously reported catalytic performance of different transition metal based catalyst selenation reaction between bromobenzene with diselinide reagent or selenium powder.

S.No	Catalyst	Solvent	Base	Additive	Catalyst (mol%)	Temp (°C)	Time (hrs)	Yield (%)	Ref
1	CuI-bpy	DMF	Na_2CO_3	Al, MgC	15	110	24	84	[32]
2	Cu-TC	DMSO	-	bipy	20	120	20	80	[33]
3	CuNPs/AC	DMSO	-	-	10	100	6	97	[46]
4	CuO	DMSO	Na_3PO_4	-	10	110	24	92	[47]
5	CuO NPs	DMSO	KOH	-	10	90	2	96	[48]
6	$PdCl_2(NCPh)$	DMSO	-	-	10	120	12	85	[49]
7	$Ni(OAc)_2$	DMF	Na_2CO_3	PPh_3	10	120	24	95	[50]
8	$CuCl_2$	DMF	Na_2CO_3	-	10	140	24	85	[51]
9	$Cu(OAc)_2$	Toluene	K_2CO_3	1,10-Phe	15	150	24	92	[52]
10	-	H_2O	KOH	TBAI	-	45	12	82	[53]
11	Pd@TATAM	DMSO	K_3PO_4	-	0.5	100	6	84	**Present -work**

Conclusions

In summary, we have demonstrated a facile synthesis of nitrogen containing covalent triazine polymer which have developed from condensation reactions between melamine and 4,4',4''-(1,3,5-Triazine-2,4,6-triyl)tribenzaldehyde of commercially available and cheap starting materials under solvothermal conditions. The CTPs have an accessible surface area, pore size and good solid support for palladium NPs and Pd@TATAM with efficient, recyclable heterogeneous catalytic activity towards mono selenation of arylhalide C-Se coupling reactions to performed K_3PO_4 base, dimethylsulfoxide as a solvent at 100 °C for about 6 hrs. The C-Se coupling reaction was using elemental selenium powder act as a selenating agent. In addition, the reaction was carried out in the absence of any additional stabilizes ligand and also we got a very good product yield over a very short reaction time. The reaction system shows tolerance toward numerous substituted arylhalide to obtain the corresponding products in good to excellent yield, the reactions employs environmentally friendly solvent and no additives/inert atmosphere/ligand free protocol.

Experimental section

Materials and methods

All the chemicals and reagents were purchased from commercial reagent suppliers, used without further purification as commercially available unless otherwise noted. All the solvents were obtained from laboratory reagent grade. The ^1H and ^{13}C NMR spectra were recorded on a Bruker (Avance) 300 and 400 MHz NMR instrument using TMS as an internal standard and $CDCl_3$ as a solvent. Chemical shifts are given in ppm (δ-scale) and the coupling constants are given in Hz. ^{13}C CP-MASNMR was recorded using a Burker Avance 500 MHz operating at 75 MHz for ^{13}C nuclei. The thermal stability of the samples were evaluated by TGA (SCINCO thermal gravimeter S-1000, Japan) under the Argon (Ar) atmosphere over the temperature range upto 30-800 ^oC, in flowing argon gas at heating rate of 5 ^oC min^{-1}. Powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku diffractometer using CuKα (λ =1.5404 Å) source with a scan rate of 0.5^o min^{-1}. The N_2 adsorption-desorption isotherms were measured on a

BELsorp-Max (BEL, Japan) at 77 K. The surface area of the samples was calculated by using the Brunauer–Emmett–Teller (BET) method and the pore sizes of the samples were calculated using the NL-DFT model. The morphology and particle size of the polymerized materials were examined by SEM and TEM. The scanning electron microscopy (SEM) measurements were performed by VEGA3 TESCAN, CZECH REPUBLIC. Energy dispersive X-ray spectroscopy (EDX) was carried out using Bruker Nano, Germany. The FT-IR spectra were obtained from a JASCO FT/IR-410 spectrometer. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of n-hexanes and ethyl acetate as an eluent. Column chromatography was carried out on silica gel (60-120 mesh) using n-hexanes and ethyl acetate as an eluent.

Synthesis of TATAM polymer

A 100 mL Schlenk tube was charged with melamine (30 mg, 0.13 mmol) and 15 mL (1:2) of dioxane/DMSO mixture, and stirred well under nitrogen atmosphere. The resultant homogeneous solution was treated with drop wise addition of 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tribenzaldehyde (100 mg, 0.132 mmol) dissolved in anhydrous THF (2 mL) and then finally glacial acetic acid (6 M) was slowly added during this course of the reaction until the colorless homogeneous solution was appeared. The reaction tube was capped tightly and then transferred to oil bath, heated at 150 °C for about 3 days. After completion of the reaction, the mixture was poured into 100 mL of water and stirred for 2 hrs, the colorless solid was completely settled in the bottom of aqueous solution. In addition, the solid was filtered and subsequently washed with water, DMF, acetone, THF, DCM, to remove the unreacted starting materials. After that, the solid was immersed in acetone for one day and filtered, then dried at 80 °C under the vacuum oven for 8 hrs to get 85% yield of colorless solid product. FT-IR (powder cm^{-1}) 3325, 1640, 1546, 1490, 1341, 1127, 1034, 876, 783, 614. Elemental analysis calculated from EDS analysis (Atomic %) for $C_{27}N_{13}H_{15}$:C 52.31, N 37.27, H 3.45; found C 46.94, N 38.06, O 13.29, H 3.02.

Synthesis of Pd@TATAM polymer

To a stirred solution of solid TATAM (100 mg) was dispersed methanol (15 mL) in a 25 mL round bottom flask. $PdCl_2$ (20 mg) was added into the reaction mixture then stirred at room temperature for 30 minutes, meanwhile the colorless solid was changed to light brown color. After that, the reducing agent hydrazine monohydrate (100 μL) was subsequently added into the reaction mixture and also maintained constant stirring for about 6 hrs, and then filtered, washed with methanol (3 × 20 mL), acetone (3×20 mL) and water to remove the unreacted $PdCl_2$. In addition, the solid was dried in a vacuum oven at 70 °C for 8 hrs to obtain Pd@TATAM as a light black colored powder (93 mg, 93% yield). FT-IR (powder cm^{-1}) 3342, 1652, 1520, 1490, 1201, 1117, 1043, 810, 783, 614; Elemental analysis calculated from EDS analysis (Atomic %) for C 48.42, N 37.09, O 12.47, Pd 0.65.

General procedure for selenation of Aryl halide to C-Se coupling reactions

Aryl bromide (1 mmol), elemental selenium (1 mmol), K_3PO_4 (1.5 mmol), Pd@TATAM (20 mg) were taken in DMSO and the reaction mixture was stirred at 100°C for about 6 hrs. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with 5 mL ethyl acetate and then the catalyst was removed by simple filtration through celite bed. The filtrate was washed with brine solution and extracted with an excess amount of ethyl acetate and then concentrated under reduced pressure. The crude product was further purified by silica gel (60-120 mesh) column chromatography (petroleum ether/ethyl acetate) to afford the corresponding diarylmonoselinide and tiny amount of homo coupled byproduct was observed.

Acknowledgments

AS and VS acknowledge the financial support of the Department of Science and Technology, SERB, Extramural Major Research Project (Grant No. EMR/2015/000969), Council of Scientific and Industrial Research (CSIR), HRDG, No. 01(2901)/17/EMR-II, New Delhi, Department of Science and Technology DST/TM/CERI/C130(G), New Delhi, India.

Keywords: Melamine, Elemental selenium, Diarylmonoselinide, Monoselinide, Solvothermal.

References

[1] P. Puthiaraj, S. M. Cho, Y. R. Lee, W. S. Ahn, *J. Mater. Chem. A*, **2015**, *3*, 6792-6797.

[2] L. Stegbauer, K. Schwinghammer, B. V. Lotsch, *Chem. Sci.*, **2014**, *5*, 2789-2793.

[3] H. Furukawa, O. M. Yaghi, *J. Am. Chem. Soc.*, **2009**, *131*, 8875-8883.

[4] S. B. Kalidindi, H. Oh, M. Hirscher, D. Esken, C. Wiktor, S. Turner, G. V. Tendeloo, R. A. Fischer, *Chem. Eur. J.*, **2012**, *18*, 10848-10856.

[5] Z. Li, X. Feng, Y. Zou, Y. Zhang, H. Xia, X. Liu, Y. Mu, *Chem. Commun.*, **2014**, *50*, 13825-13828.

[6] S. Wan, F. Gandara, A. Asano, H. Furukawa, A. Saeki, S. K. Dey, L. Liao, M. W. Ambrogio, Y. Y. Botros, X. Duan, S. Seki, J. F. Stoddart, O. M. Yaghi, *Chem. Mater.*, **2011**, *23*, 4094-4097.

[7] P. Puthiaraj, W. Seung Ahn, *Catal. Commun.*, **2015**, *65*, 91-95.

[8] P. Puthiaraj, S. Sung Kim, W. Seung Ahn, *Chem. Eng. J.*, **2016**, *283*, 184-192.

[9] P. Puthiaraj, K. Pitchumani, *Chem. Eur. J.*, **2014**, *20*, 8761-8770.

[10] C. J. Doonan, D. J. Tranchemontagne, T. G. Glover, J. R. Hunt, O. M. Yaghi, *Nat. Chem.*, **2010**, *2*, 235-238.

[11] N. L. Campbell, R. Clowes, L. K. Ritchie, A. I. Cooper, *Chem. Mater*., **2009**, *21*, 204-206.

[12] S. Y. Ding, W. Wang, *Chem. Soc. Rev*., **2013**, *42*, 548-568.

[13] Q. Fang, S. Gu, J. Zheng, Z. Zhuang, S. Qiu, Y. Yan, *Angew. Chem. Int. Ed*., **2014**, *53*, 2878-2882.

[14] L. Xu, L. Cao, Z. Guo, Z. Zha, S. Lei, *Chem. Commun*., **2015**, *51*, 8664-8667.

[15] F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klock, M. OKeeffe, O. M. Yaghi, *J. Am. Chem. Soc*., **2009**, *131*, 4570-4571.

[16] K. Sakaushi, M. Antonietti, *Acc. Chem. Res*., **2015**, *48*, 1591-1600.

[17] J. Long, H. Liu, S. Wu, S. Liao, Y. Li, *ACS Catal*., **2013**, *3*, 647-654.

[18] C. E. Chan-Thaw, A. Villa, P. Katekomol, D. Su, A. Thomas, L. Prati, *Nano Lett*., **2010**, *10*, 537-541.

[19] P. Kuhn, M. Antonietti, A. Thomas, *Angew. Chem., Int. Ed*., **2008**, *47*, 3450-3453.

[20] M. J. Bojdys, J. Jeromenok, A. Thomas, M. Antonietti, *Adv. Mater*., **2010**, *22*, 2202-2205.

[21] P. Katekomol, J. Roeser, M. Bojdys, J. Weber, A. Thomas, *Chem. Mater*., **2013**, *25*, 1542-1548.

[22] R. Palkovits, M. Antonietti, P. Kuhn, A. Thomas, F. Schuth, *Angew. Chem., Int. Ed*., **2009**, *48*, 6909-6912.

[23] V. Sadhasivam, R. Balasaravanan, C. Chithiraikumar, A. Siva, *chemistry select*, **2017**, 2, 1063-1070.

[24] P. Puthiaraja, K. Pitchumani, *Green Chem*., **2014**, *16*, 4223-4233.

[25] R. Imran Khana, K. Pitchumani, *Green Chem*., **2016**, *18*, 5518-5528.

[26] S. Patai, Z. Rappoport, *The Chemistry of Organic Selenium and Tellurium Compounds*, John Wiley & Sons: New York, Vol *1*, 1986-1987.

[27] A. M. Faucher, P. W. White, C. Brochu, C. G. Maitre, J. Rancourt, G. Fazal, *J. Med. Chem.* **2004**, *47*, 18-21.

[28] E. G. Hope, W. Levason, *Coord. Chem. Rev*., **1993**, *122*, 109-170.

[29] M. Bonaterra, S. E. Martın, R. A. Rossi, *Tetrahedron Lett*., **2006**, *47*, 3511-3515.

[30] T. Chatterjee, B. C. Ranu, *J. Org. Chem.* **2013**, *78*, 7145-7153.

[31] B. Mohan, C. Yoon, S. Jang, K. H. Park, *ChemCatChem*., **2015**, *7*, 405-412.

[32] N. Taniguchi, *Synlett.*, **2005**, *11*, 1687-1690.

[33] F. Shibahara, T. Kanai, E. Yamaguchi, A. Kamei, T. Yamauchi, T. Murai, *Chem. Asian J.* **2014**, *9*, 237-244.

[34] D. Luo, G. Wu, H. Yang, M. Liu, W. Gao, X. Huang, J. Chen, H. Wu, *J. Org. Chem.*, **2016**, *81*, 4485-4493.

[35] M. G. Schwab, B. Fassbender, H. W. Spiess, A. Thomas, X. Feng, K. Mullen, *J. Am. Chem. Soc*., **2009**, *131*, 7216-7217.

[36] Y. Borodko, H. S. Lee, S. H. Joo, Y. Zhang, G. Somorjai, *J. Phys. Chem. C*, **2010**, *114*, 1117-1126.

[37] D. S. Ruby Josephine, B. Sakthivel, K. Sethuraman, A. Dhakshinamoorthy, *Chemistry Select*, **2016**, *1*, 2332-2340.

[38] P. Puthiaraj, W. Ahn, *Ind. Eng. Chem. Res.*, **2016**, *55*, 7917-7923.

[39] J. C. Park, E. Heo, A. Kim, M. Kim, K. H. Park, H. Song, *J. Phys. Chem. C*, **2011**, *115*, 15772-15777.

[40] M. Shunmughanathan, P. Puthiaraj, K. Pitchumani, *ChemCatChem*, **2015**, *7*, 666-673.

[41] G. Yang, H. Han, C. Du, Z. Luo, Y. Wang, *Polymer*, **2010**, *51*, 6193-6202.

[42] A. C. Thomas, *Photoelectron and Auger Spectroscopy, Plenum*, New York, **1975**, 352.

[43] J. Huang, J. Yin, W. Chai, C. Liang, J. Shen, F. Zhang, *New J. Chem.*, **2012**, *36*, 1378-1384.

[44] J. Wei, P. Hing, Z. Q. Mo, *Surf. Interface Anal.*, **1999**, *28*, 208-211.

[45] I. P. Beletskaya, V. P. Ananikov, *Chem. Rev.*, **2011**, *111*, 1596-1636.

[46] B. Mohan, C. Yoon, S. Jang, K. Hyun Park, *ChemCatChem.*, **2015**, *7*, 405-412.

[47] D. Luo, G. Wu, H. Yang, M. Liu, W. Gao, X. Huang, J. Chen, H. Wu, *J. Org. Chem.*, **2016**, *81*, 4485-4493.

[48] D. Singh, A. M. Deobald, L. R. S. Camargo, G. Tabarelli, O. E. D. Rodrigues, A. L. Braga, *Org. Lett.*, **2010**, *12*, 3288-3291.

[49] M. Iwasaki, Y. Tsuchiya, K. Nakajima, Y. Nishihara, *Org. Lett.*, **2014**, *16*, 4920-4923.

[50] M. Iwasaki, N. Miki, Y. Tsuchiya, K. Nakajima, Y. Nishihara, *Org. Lett.*, **2017**, *19*, 1092-1095.

[51] D. Hu, M. Liu, H. Wu, W. Gao, G. Wu, *Org. Chem. Front.*, **2018**, *5*, 1352-1355

[52] J. Wang, H. Li, T. Leng, M. Liu, J. Ding, X. Huang, H. Wu, W. Gaob, G. Wu, *Org. Biomol. Chem.*, **2017**, *15*, 9718-9726.

[53] G. Wu, L. Min, H. Li, W. Gao, J. Ding, X. Huang, M. Liu, H. Wu, *Green Chem.*, **2018**, *20*, 1560-1563.