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# Triazine functionalized ordered mesoporous polymer: a novel solid support for Pd-mediated C–C cross-coupling reactions in water<sup>†</sup>

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A new functionalized mesoporous polymer (MPTAT-1) has been synthesized *via* organic–organic radical polymerization of 2,4,6-triallyloxy-1,3,5-triazine (TAT) in aqueous medium in the presence of an anionic surfactant (sodium dodecyl sulfate) as template. Powder XRD and TEM image analysis suggests the presence of ordered 2D-hexagonal arrangement of pores in the material. N<sub>2</sub> sorption analysis reveals a moderately good surface area  $135 \text{ m}^2 \text{ g}^{-1}$  for this mesoporous polymer. The template free MPTAT-1 acts as an excellent support for immobilizing Pd(II) at its surface and the resulting material showed very good catalytic activity in several C–C cross-coupling reactions like Mizoroki–Heck, Sonogashira and Suzuki–Miyaura in an environmentally benign reaction medium, water. The catalyst exhibits very high catalytic activity for the coupling of various aryl halides including aryl chlorides with alkenes or alkynes and the sodium salt of (trihydroxy)phenylborate. Due to strong binding with the functional groups of the polymer, the anchored Pd(II) could not leach out from the surface of the mesoporous catalyst during the reaction and it has been reused several times without appreciable loss in catalytic activity.

# Introduction

Since the first discovery of ordered mesoporous silicas<sup>1</sup> these materials have attracted widespread attention in both academics and industry due to their huge potential applications.<sup>2</sup> Today mesoporous materials have been employed successfully in gas adsorption<sup>3</sup> and storage,<sup>4</sup> ion-exchange,<sup>5</sup> catalysis,<sup>6</sup> sensing,<sup>7</sup> and so on. In general, these materials can be synthesised by means of a soft templating route using either a cationic or anionic surfactant as the structure directing agent<sup>1,8</sup> or by a hard templating approach, such as those employing colloidal particles.9 Removal of surfactant molecules through solvent extraction produces functionalized mesopores having tuneable pore dimensions, which can act as a scaffold for the synthesis of nanomaterials due to the presence of active functional groups at the mesopore surface. To date, mesoporous materials composed of inorganic oxides10 and inorganic-organic hybrid silica11 materials have been studied extensively, but very limited research work has been carried out on purely organic mesoporous materials prepared through a surfactant templating pathway.<sup>12</sup> Purely organic mesoporous materials synthesized through a

surfactant templating route can carry suitable functional groups at their surface, which can effectively interact with relevant metal ion/molecules and therefore are potential candidates for heterogeneous catalysts.<sup>13</sup>

In this context it is pertinent to mention that palladium catalysed C-C cross-coupling reactions like Suzuki, Heck, Sonogashira, are extremely important from the synthetic organic chemistry point-of-view.14 One of the most challenging tasks in organic chemistry today is to design efficient and eco-friendly catalysts for C-C bond formation reactions. Homogenous Pdcatalysts used in these reactions have several draw backs due to tedious and time consuming work-up procedures associated with inefficient recycling. A heterogeneous Pd-catalyst can solve these problems very efficiently and thus supported Pd-catalysts can offer high activity and selectivity in the C-C coupling reactions.15 Thus it is highly desirable to develop an efficient supported Pdcatalyst based on a functionalized mesoporous material. Functionalized mesoporous silica, metal-organic frameworks, resins, gels, metal oxides, clays etc., containing suitable binding sites could serve as the desired heterogeneous matrix for the binding of active metal centres and thus subsequent used in catalytic reactions.16 However, only very limited number of materials can be used as a catalyst in the presence of water as the reaction medium,<sup>17</sup> which is most environmentally benign solvent. Most of these C-C coupling reactions proceed in the presence of environmentally hazardous solvent like DMF, DMSO, THF or acetonitrile etc. So, designing a new catalyst and grafting it with active metal centres to explore its potential application in

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C–C coupling reactions in water is very demanding. Herein, we first report the synthesis of a new ordered mesoporous polymer containing 2,4,6-triallyloxy-1,3,5-triazine moiety, grafted with Pd(II) at its surface and its use in Heck, Sonogashira and Suzuki C–C cross-coupling reactions maintaining eco-friendly conditions.

# **Experimental section**

#### Materials

2,4,6-Triallyloxy-1,3,5-triazine (TAT, monomer), palladium acetate, styrene, phenyl acetylene and other reactants for the catalytic reactions were obtained from Sigma Aldrich. N,N,N',N'tetramethylethylenediamine (TMED, promoter), ammonium persulfate (APS, radical initiator), sodium dodecyl sulfate (SDS, template) were purchased from Loba Chemie. All other chemicals used for this investigation purposes were of analytical grade produced by E-Merck, unless mentioned otherwise.

#### Instrumentation

Carbon, hydrogen and nitrogen contents of both the mesoporous polymer and Pd-grafted polymer were analyzed using a Perkin Elmer 2400 Series II CHN analyzer. X-Ray diffraction patterns of the powder samples were obtained with a Bruker AXS D8 Advanced SWAX diffractometer using Cu-Kα (0.15406 nm) radiation. N<sub>2</sub> adsorption/desorption isotherms of the samples were recorded using Bel Japan Inc. Belsorp-HP at 77 K. Prior to the measurement, the samples were degassed at 393 K for 12 h under high vacuum conditions. Transmission electron microscopy (TEM) images of the mesoporous polymer were obtained using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. The samples were prepared by dropping a colloidal solution onto the carbon-coated copper grids. Scanning electron microscopic measurements were performed with a JEOL JEM 6700F field-emission scanning electron microscope (FESEM). Pd content was determined by atomic absorption spectroscopic (AAS) analysis by using a Shimadzu AA-6300 AAS spectrometer fitted with a double beam monochromator. UV-visible diffuse reflectance spectra were recorded on a Shimadzu UV 2401PC with an integrating sphere attachment. BaSO<sub>4</sub> was used as the background standard. FT-IR spectra of these samples were recorded using a Nicolet MAGNA-FT IR 750 Spectrometer Series II.

# Synthesis of mesoporous poly-2,4,6 -triallyloxy-1,3,5-triazine (MPTAT-1)

MPTAT-1 has been synthesised through the aqueous-phase polymerisation of 2,4,6-triallyloxy-1,3,5-triazine (TAT) under hydrothermal condition by using ammonium persulfate (APS) as an initiator. In a typical synthesis, 2.35 g (0.00814 mol) of SDS was dissolved in 40 ml of water with constant stirring followed by the addition of 2 g (0.008 mol) of 2,4,6-triallyloxy-1,3,5-triazine. After the addition of 0.94 g (0.00814 mol) of TMED to this mixture, concentrated HCl (12 N) was added dropwise to obtain a clear solution. This helps the protonation of the *N*-atoms of the TAT molecules, which facilitates the ionic interaction with the negative charge of  $C_{12}H_{23}SO_3^-$  of the SDS

molecules. The pH of the gel was maintained at *ca*. 7.0. Finally, 5.2 g (0.016 mol) of APS dissolved in 10 ml of distilled water was added quickly into the solution with vigorous stirring. A white precipitate appeared immediately after the addition of APS. The resultant slurry was stirred for another 3 h at room temperature and then autoclaved at 348 K for 3 days without stirring. The final pH of the synthesis gel was *ca*. 4.0–5.0. After aging, the resultant precipitate was filtered, washed thoroughly with de-ionized water, yielding mesoporous polymer MPTAT-1. The surfactant was removed from the synthesised material by extraction of 1.0 g of the MPTAT-1 material with 0.5 g acetic acid taken in 50 ml water under 4 h stirring at room temperature. This template extraction procedure was repeated three times to obtain template-free MPTAT-1.

# Synthesis of palladium grafted mesoporous poly-2,4,6-triallyloxy-1,3,5-triazine (Pd-MPTAT-1)

Synthetic procedure for grafting of palladium onto the mesoporous poly-2,4,6-triallyloxy-1,3,5-triazine (MPTAT-1) has been illustrated in Scheme 1. For Pd loading, 1.0 g of the template-free mesoporous polymer was taken in a round bottom flask and it was dispersed in 25 ml of glacial acetic acid. To this 0.5 g palladium acetate was added and the suspension was refluxed for about 12 h under a nitrogen atmosphere with vigorous stirring until the colour changed to black. At the end, the resulting dark solid was filtered and washed thoroughly with THF, methanol and acetone, and finally dried under vacuum for 24 h to obtain Pd-MPTAT-1.



Scheme 1 Organic–organic *in situ* radical polymerization of 2,4,6-triallyloxy-1,3,5-triazine by APS using a SDS template and grafting on Pd(II) in acetic acid medium.

#### **Catalytic reactions**

The catalytic activity of this Pd grafted MPTAT-1 polymer has been tested for several C-C cross-coupling reactions like Mizoroki-Heck, Sonogashira, Suzuki-Miyaura in environmentally benign conditions. For the Mizoroki-Heck coupling reaction, 1 mmol of arylhalide, 2 mmol of potassium carbonate ( $K_2CO_3$ ) were mixed with 10 mL water along with 5 ml ethanol and placed in a batch reactor. To this 0.02 g of Pd-MPTAT-1 polymer catalyst was added, and the mixture was heated to 110 °C in an oil bath with continuous stirring. Finally 1.5 mmol of styrene/acrylic acid was added to start the coupling reaction. For less reactive aryl chlorides 2 mmol of a phase transfer catalyst (TBAB)<sup>31</sup> was added in addition to our Pd-MPTAT-1 catalyst. The progress of the reaction was monitored by TLC and it has been found that 10-12 h is required for full conversion of aryl iodides and bromides, but a much longer reaction time such as 20-24 h is required for less reactive aryl chloride coupling. For isolation of the products at the end of each catalytic reaction, the heterogeneous catalyst was first separated out by filtration, then the filtrate was evaporate by a rotary evaporator to remove ethanol and finally the concentrated part was extracted with ethyl acetate  $(3 \times 20 \text{ ml})$  and thoroughly washed with water and brine solution. The organic layer was collected and dried over Na<sub>2</sub>SO<sub>4</sub>, and finally the remaining solvent was removed under vacuum at 25 °C. Crude product was isolated and repeatedly re-crystallized from ethyl acetatehexane mixture to obtain compounds having sufficient purity for further characterization purposes.

Use of Pd-MPTAT as catalyst for Sonogashira cross-coupling reaction in triethanol amine has been carried out without addition of any external base or solvent. Thus in a typical synthesis, 1.0 mmol of arylhalide, 0.05 mmol of CuI were mixed with 12 mL of triethanol amine and placed in a batch reactor. To this solution 0.02 g of Pd-MPTAT-1 was added. The mixture was then heated to 80 °C in an oil bath under nitrogen atmosphere with continuous stirring. The coupling reaction started immediately after addition of 1.5 mmol phenylacetylene to the mixture. The progress of the coupling reaction was monitored by TLC and it took 8-12 h for complete conversion depending on the substrate. For isolation of the products at the end of the catalytic reaction, the catalyst was first separated out by filtration and thoroughly washed with water and hexane. The filtrate was then extracted with hexane three times  $(3 \times$ 20 ml) and finally washed with brine. The organic layers thus collected were combined and dried over anhydrous MgSO4. Solid compounds were obtained on evaporation of the organic solvent under vacuum at 25 °C. The crude products were repeatedly re-crystallized from hot ethanol to obtain purified products.

We carried out the Suzuki–Miyaura cross-coupling reaction using sodium salt of phenyl trihydroxyborate<sup>18</sup> as the coupling agent, instead of using conventional phenyl boronic acid, with aryl halides in water under base-free conditions. In a typical synthesis, 1 mmol aryl halide, 1.2 mmol phenyl trihydroxyborate were taken in a round bottom flask. The flask was charged with 5:1 (by volume) mixture of water–DMF and 0.02 g catalyst. The mixture was refluxed at 90 °C with continuous stirring. Progress of the reaction was monitored by using TLC technique. It took 8–10 h for completion of reaction. At the end of the reaction, the catalyst was first separate out by filtration, and this is followed by washing with water and diethylether. The filtrate was extracted thrice with 1:1 mixture of diethyl ether and hexane (3 × 20 ml). The crude product was repeatedly re-crystallized from pet-ether/ethyl acetate to obtain compounds having sufficient purity which were further characterized by NMR spectroscopy. The products were isolated, purified and then identified by <sup>1</sup>H NMR, <sup>13</sup>C NMR, FTIR, CHN analysis *etc.* methods. Melting points of those compounds are in good agreement with those reported in literature. NMR spectra were measured on a Bruker Avance DPX 300 NMR (300 MHz) spectrometer using TMS as the internal standard. The detail experimental procedures of the individual coupling reactions are given below.

### **Results and discussion**

#### Formation of mesophase

In the presence of the anionic structure directing agent SDS, organic-organic supramolecular assembly takes place in aqueous medium. At the acidic pH conditions the positively charged protonated *N*-atoms of the triazine moiety preferentially interact with the negatively charged polar head groups *i.e.*  $C_{12}H_{23}SO_{3}^{-}$  and condensed around the micelle to form a continuous mesophase. The resulting array of organic mesophases upon removal of the surfactant by acid extraction retains its mesoporous structure. In Scheme 1 we have described the polymerisation of TAT monomer in the presence of ammonium persulfate, which is a good radical initiator for aqueous phase polymerisation of olefins under mildly acidic condition.<sup>20</sup> Since one monomer contains three olefinic double bonds in each of its branches, its polymerisation gives random cross-linking, leading to a highly stable and robust organic framework.

Immobilization of palladium and its strong binding at the MPTAT-1 surface has been facilitated due to the presence of strong donor sites in the triazine moiety.<sup>11d</sup>

#### Mesophase

In Fig. 1 small angle powder diffraction patterns of both (a) the as synthesized MPTAT-1 and (b) the template-free MPTAT-1 are shown. For as synthesized sample, in addition to a large diffraction peak at 2 $\theta$  ca. 2.0, two additional weak intensity peaks suggesting the presence of ordered mesophase.<sup>21,22</sup> The template-free sample shows one strong peak at  $2\theta = 2.08$ , which indicates little contraction of pore wall upon removal of template from the as synthesized polymer. A transmission



Fig. 1 XRD patterns of (a) the synthesized and (b) acid extracted MPTAT-1.



Fig. 2 Transmission electron micrograph of MPTAT-1.

electron microscopic image of MPTAT-1 is shown in Fig. 2. In this image low electron density spots (pores) were seen throughout the specimen and these are arranged in a honeycomb like 2D-hexagonal array. The average pore diameter as estimated from the HR TEM image was ca. 3.8 nm, which agrees reasonably well with other mesoporous materials synthesized through anionic SDS templating route.<sup>23</sup> The pore dimension of this material was further confirmed from the FFT pattern as shown in the inset of the Fig. 2. Bright diffraction spots and their hexagonal arrangement were quite clear. This HR TEM image also reveals a wall thickness of ca. 1.1 nm. Well defined spherical external morphologies of this material were observed from the corresponding FE SEM image as shown in Fig. 3. The particles are spherical in nature and have a diameter of ca. 50 nm. These nanospheres adhere among themselves at the surface to form large aggregated particles, which could be due to the random polymerisation of the 2,4,6-triallyloxy-1,3,5-triazine monomer.

#### Porosity and surface area

In Fig. 4 nitrogen adsorption/desorption isotherms of the template-free MPTAT-1 are shown. This isotherm is closely related to a type IV isotherm, characteristic of mesoporous materials.24 However, in contrast to the sharp capillary condensation usually observed for mesoporous solids, here a gradual and very broad uptake of N2 occurred over the entire high  $P/P_0$  scale. From the nitrogen sorption isotherm BET surface area of the sample was found to be 135 m<sup>2</sup> g<sup>-1</sup>. In this context it is pertinent to mention that a purely organic mesoporous polymer usually has a small surface area,<sup>25</sup> whereas inorganic mesoporous materials and organic-inorganic hybrid mesoporous materials have a high surface area.<sup>11,26</sup> Pore size distribution (PSD) of the sample MPTAT-1, is shown in the inset of Fig. 4 employing NLDFT (non-local density functional theory) method. From this PSD, a broad distribution having maximum pore width of 3.7 nm is observed.

# Characterization of Pd-MPTAT-1 catalyst

Due to the insolubility of Pd-MPTAT-1 in all common organic solvents, its structural investigation was limited to only phsico-



5.0kV X50,000 100nm WD 9.7mm



Fig. 3 Scanning electron micrographs of MPTAT-1 (a) and Pd-MPTAT-1 (b).

chemical properties like UV-visible absorbance, SEM-EDX, TEM, FTIR, CHN analysis, AAS etc. Elemental analysis reveals the presence of C, H, and N contents in this mesoporous polymer before and after loading of Pd. It was found that the MPTAT-1 before loading possesses C = 54.89%, H = 7.93%, N = 10.39%, whereas in Pd-MPTAT-1 it was C = 52.33%, H = 6.55%, N =10.3%. Retention of C. H. N contents confirm the stability of the triazine framework under very drastic conditions such as glacial acetic acid during metal loading. The metal (Pd) content of polymer anchored Pd(II) complex as determined by AAS suggested 5.16 wt%, and for 0.02 g of Pd-MPTAT-1 catalyst, the loading of Pd was supposed to be 0.8 mol% with respect to 1 mol reactant, which is in good agreement with the amount of Pdcatalyst used (0.25-3 mol% Pd) in the reports on Pd-mediated cross-coupling reactions.<sup>27,28</sup> FT IR spectra of both mesoporous polymers MPTAT-1 and Pd-MPTAT-1 are shown in Fig. 5. Both the samples showed two distinct C-H vibrations in the region 2932-2950 cm<sup>-1</sup>, corresponding to non-identical C-H bonds in



**Fig. 4**  $N_2$  adsorption/desorption isotherms of MPTAT-1 at 77 K. Adsorption points are marked by filled circles and desorption points by empty circles. Pore size distribution is shown in the inset.



Fig. 5 FTIR spectra of MPTAT-1 (a) and Pd-MPTAT-1 (b).

the triazine framework. Further mesoporous polymer sample (a) exhibits very strong and broad absorption band at 3435 cm<sup>-1</sup>, which is mainly due to N-H stretching. After Pd loading, in sample (b), this band at 3435 cm<sup>-1</sup> diminished in intensity and slightly shifted towards the lower frequency region. Both samples (a) and (b) exhibited very strong band at 1563 cm<sup>-1</sup> due to ring >C=N stretching vibration and two additional sharp peaks at 1142 cm<sup>-1</sup> ( $v \sim C-N$ ) and 1420 cm<sup>-1</sup> ( $v \sim CH_2$ ). Further, the allylic double bond (-C=C-) stretching of 2,4,6-triallyloxy-1,3,5-triazine moiety at 1840 cm<sup>-1</sup>, has disappeared and the intensity of another at 1714 cm<sup>-1</sup> has diminished considerably, suggesting near completion of polymerization reaction. Thus these framework vibrations suggested the presence of 2,4,6triallyloxy-1,3,5-triazine moiety in MPTAT-1 and Pd-MPTAT materials. Further, UV absorbance spectra (Fig. 6a) of MPTAT-1 exhibits no strong characteristic absorbance, except two very weak peaks at 207 and 266 nm due to very weak  $\pi \rightarrow \pi^*$  transitions. But a distinguishable change in absorbance is observed in case of Pd-MPTAT-1 material. The UV-visible absorbance spectrum of this Pd-grafted polymer shows different strong peaks at 212, 251, 290, 362 and 645 nm. The low-spin Pd(II) complex may exhibit three spin-allowed d-d transitions from the lower lying  $d_z^2$  orbital to the higher empty  $d_x^2 d_y^2$  orbital. The bands are observed at 212 nm, 251 nm and 290 nm, which may be designated as  ${}^{1}A_{1g} \rightarrow {}^{1}Eg$ ,  ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$  transitions



Fig. 6 UV-Visible absorbance of MPTAT-1 (a) and Pd-MPTAT (b).

respectively<sup>29,30</sup> (Fig. 6b). The presence of a high coordinating ligand like triazine around Pd(II) actually shift those absorbance band towards the higher frequency region resulting in a slight deviation from theoretical values. Another strong absorbance at 645 nm *i.e.* in the visible region may be due to a change in  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions after Pd grafting in MPTAT-1. Based on those results such as elemental analysis, FTIR, UVvisible absorbance, it can be said that triazine moiety has been incorporated into the polymeric framework of MPTAT-1.

## Catalysis

Pd-MPTAT-1 acts as a very efficient catalyst in C–C coupling reactions of different aryl halides. The reaction shows good diversity in the presence of both electron donating and electron withdrawing groups. In the following three sections we have described C–C coupling reactions over Pd-MPTAT-1.

a) Pd-MPTAT-1 catalysed Mizoroki–Heck cross-coupling in water–ethanol mixture. Pd-MPTAT-1 catalyst exhibits very high catalytic activity and *trans*-selectivity in Mizoroki–Heck cross-coupling in water. Since from its discovery in early 1970s, Heck–Mizoroki cross-coupling has been widely used as a tool in organic synthesis because of the direct incorporation of the olefin moiety in the aromatic framework.<sup>15</sup> This method has been conveniently applied to total synthesis in organic chemistry because of the tolerance of several functional groups, without the need to protect them. Several supported Pd-nanoparticles<sup>31</sup> and Pd-immobilized mesoporous silica<sup>32</sup> are found to serve for that purpose, but a very few of them can be applied in water, which is most desirable eco-friendly solvent. Our Pdcontaining mesoporous catalyst can be very efficiently utilized in water-ethanol mixed solvent system. Results are summarized in Table 1, which shows that Pd-MPTAT-1 is active for a variety of functional groups, yielding only E-selective coupling products. It has been observed that the reaction goes well not only with aryl iodides and bromides but also with aryl chlorides. However, the yield of the coupling product for aryl chlorides are somewhat lower and requires a prolonged time compare to their bromo and iodo analogues. Coupling of aryl chlorides in water has been carried out in presence of a phase transfer agent such as NBu<sub>4</sub>Br (tetrabutyl ammonium bromide).<sup>33</sup> The reaction was conveniently carried out at 110 °C for bromo- and iodobenzenes but for activation of chlorobenzene, a higher temperature at about 150 °C is required. Lowering in temperature often results in incomplete conversion of the starting materials. Several organic and inorganic bases were screened and it was observed that K<sub>2</sub>CO<sub>3</sub> was the most efficient base for our present catalytic system in water-ethanol mixture. Other inorganic and organic bases were not as effective as K<sub>2</sub>CO<sub>3</sub>. With these optimised reaction conditions the coupling of various substituted and non-substituted aryl halides with styrene and acrylic acid were examined to explore the scope and generality of this catalyst. A controlled experiment was performed in a batch using iodobenzene, styrene, K2CO3 in water-ethanol mixture without addition of our catalyst. No conversion of iodobenzene again strengthens the novelty of our catalyst. A detailed catalytic cycle has been shown schematically in Fig. 7, where the Heck coupling product is supposed to be formed through the intermediates A, B, C, D, E and F species at the surface of the Pd-grafted mesoporous polymer matrix.



Fig. 7 Catalytic cycle of Mizoroki–Heck cross-coupling reaction over Pd-MPTAT-1.

b) A unique approach for Sonogashira cross-coupling using Pd-MPTAT-1 catalyst. Another powerful method for C(sp)- $C(sp^2)$  cross-coupling in organic chemistry is the Sonogashira coupling,<sup>15</sup> where an aryl halide is used to couple with a terminal alkyne in the presence of a base and Pd-catalyst.

Ever since its discovery, it has had tremendous application in heterocyclic chemistry, the synthesis of natural products and pharmaceuticals<sup>34</sup> for incorporating an alkyne moiety directly in the compound. The original Sonogashira reaction often required degassed organic solvent, inert atmosphere, strong base, prolonged reaction time and phosphine containing catalyst. Here we have shown that new catalyst Pd-MPTAT-1 is efficient in this reaction under eco-friendly condition by using triethanolamine as solvent as well as base. Thus, the use of degassed organic solvent and the environmentally toxic phosphine<sup>19</sup> ligand-containing catalyst is eliminated. After judicial screening with base, solvent, temperature etc., we have observed that instead of adding additional base to the medium, triethanol amine alone can serve the dual character i.e. both as a base as well as solvent and the optimised temperature should be 90 °C for a successful completion of the coupling reaction with our present catalytic system. In the absence of 0.05 mmol equivalent CuI, the Sonogashira reaction goes well but the conversion was poor (~25%). Using CuI as the co-catalyst dramatically improves conversion for iodo and bromo compounds. However, moderate conversion was found for chlorobenzene derivatives. Using these optimized reaction conditions the efficiency of our catalyst has been investigated for Sonogashira coupling with various aryl halides and phenyl acetylene, the results are summarized in Table 2. From the experimental findings we infer that our present catalyst has very good tolerance for a wide variety of substrates. A controlled experiment using aryl halide, phenyl acetylene, CuI and triethanolamine has been performed in the absence of Pd-MPTAT-1 catalyst and the result shows practically no conversion of the reactant. All those experimental findings again suggested the catalytic role played by Pd-grafted mesoporous polymer Pd-MPTAT-1 in the coupling reaction. In Fig. 8 we have shown the possible mechanism of Sonogashira coupling schematically. Coupling between aryl halides and



**Fig. 8** Catalytic cycle of the Sonogashira cross-coupling reaction over Pd-MPTAT-1.

 Table 1
 Heck coupling of aryl halides over Pd-MPTAT-1 catalyst<sup>a</sup>



X = I, Br, CI						
Entry	Aryl halide	Product	Time (h)	Yield <sup>b</sup> (%)	Reference	
1			8	95	S1	
2	Br		10	85	S1	
3			7	95	S2	
4			10	85	S2	
5	Br COCH <sub>3</sub> Br	Сосн3	10	85	S3	
6	COCH3	Сосн3	8	90	S3	
7	OCH <sub>3</sub>	ОСН3	12	75	S4	
8	Br CH <sub>3</sub>	СН3	12	75	S5	
9	CH <sub>3</sub>	CH3	14	70	S5	
	Br					



Entry	Aryl halide	Product	Time (h)	Yield <sup>b</sup> (%)	Reference <sup>†</sup>
10	CHO Br	СНО	9	84	S7
11		СООН	6	95	S8
12	Br	СООН	8	84	S8
13		O <sub>2</sub> N-COOH	6	90	S9
14	CI		24	55	S1
15			22	60	S2
16	СНО	СНО	24	55	S7
17		O <sub>2</sub> N-COOH	20	50	S9



" Reactions were carried out using 1 mmol aryl halide, 1.5 mmol alkene, 2 mmol base, 10 ml water, 5 ml ethanol at 110 °C with 0.02 g Pd-MPTAT-1 catalyst. <sup>b</sup> Yields refer to those purified products based on <sup>1</sup>H NMR and GC analysis.

terminal alkyne has taken place through the formation of several intermediates A, B, C and through the formation of an organocopper intermediate.

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c) An alternative route for base-free Suzuki-Miyaura crosscoupling using Pd-MPTAT-1 catalyst with the sodium salt of phenyl trihydroxyborate. Suzuki–Miyaura cross-coupling<sup>15</sup> is an efficient method for C-C bond formation in organic chemistry for preparing unsymmetrical bi-aryls from aryl halide and phenyl boronic acid with tolerance over a wide range of substrates. Pd nanoparticles immobilized on solid supports are the best choice as heterogeneous catalysts for this cross-coupling reaction.35 The Suzuki cross-coupling reaction over Pd-MPTAT-1 was carried out in a mixed solvent system *i.e.* DMF and water (1:5 by volume) using aryl iodides, bromides and chlorides as substrates and the sodium salt of phenyl trihydroxyborate as an alternative to organoboron species. Using borate salt<sup>18</sup> instead of phenyl-boronic acid means phenyl boronic acid can no longer take part in the transmetalation step unless it is activated to a borate salt by employing some suitable base. Several drawbacks for a conventional Suzuki coupling using boronic acid and the external base is thus solved by using the kev intermediate directly into the reaction mixture. Dissolving phenyl boronic acid in toluene and adding concentrated NaOH solution to this mixture precipitates out the sodium salt of phenyl trihydroxyborate as a free flowing white powder. Addition of NaOH continues until the complete precipitation results. The precipitate was filtered and used for Suzuki-Miyaura coupling reactions without any further purification. Using this base-free protocol we have carried out C-C coupling reactions in water-DMF mixture (5:1), where DMF is used mainly to solubilise some typically insoluble organic halides. We have repeated the experiments to find out the best possible outcome regarding the reaction conditions by using our catalyst (Pd-MPTAT-1). So far

we found the coupling reaction proceeded well when performed in water-DMF (5:1) as the solvent in the presence of phenyl trihydroxyborate salt at 90 °C. The reaction temperature has also a significant effect for the rate of coupling. At lower temperatures (40-70 °C), low conversion was observed and increasing the temperature dramatically increases not only the reaction rate but also the yield of the final product. Thus the optimum temperature was found to be 90 °C with our present catalytic system. All results of the Suzuki-Miyaura coupling products have been summarized in Table 3. A controlled experiment was performed using bromobenzene as the substrate with the sodium salt of phenyl trihydroxyborate as organo-boron species in the absence of the catalyst (Pd-MPTAT-1). Practically no conversion of the reactant was observed, supporting the catalytic role of Pd-MPTAT-1. The result shows that the catalyst has tolerance for a wide range of substrates with different functional groups from electron donating to electron withdrawing and also to derivatives of chlorobenzene. Reactions with a chlorofunctionalized phenyl ring were not that efficient as compared with their bromo- or iodoanalogues, and require prolonged heating. Chlorobenzenes containing an electron withdrawing group require much less time for a better conversion. This has been a successful attempt by us to convert much cheaper chlorobenzene derivatives (compared to their -Br, -I analogues) to their corresponding biphenyl derivatives by using Suzuki-Miyaura cross-coupling in an environment friendly medium, water.<sup>36</sup> A schematic diagram regarding the catalytic cycle of the Suzuki-Miyaura cross-coupling has been shown in Fig. 9. The coupling product between the aryl halide and the phenyl trihydroxyborate salt proceeds through the formation of A, B, and C intermediates, at the surface of the mesoporous polymer matrix (Fig. 9). The first step is the oxidative addition of aryl halide with Pd(0) to form B. In the second step nucleophillic addition of phenyl trihydroxyborate has taken place with B

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Table 2 Sonogashira cross-coupling reaction of aryl-halides over Pd-MPTAT-1 catalyst<sup>a</sup>



<sup>*a*</sup> Reactions were carried out using 1 mmol aryl halide, 1.5 mmol alkyne, 0.05 mmol CuI, 12 ml triethanol amine under 90 °C refluxing condition with 0.02 g Pd-MPTAT-1 catalyst. <sup>*b*</sup> Yields refer to those purified products based on <sup>1</sup>H NMR and GC analysis (supporting information†).

Table 3 Base free Suzuki-Miyaura cross-coupling reaction of aryl-halides over Pd-MPTAT-1 catalyst<sup>a</sup>



R= H, -NO<sub>2</sub>, -COCH<sub>3</sub>, -CHO, -CH<sub>3</sub>, -OMe, -CN, -COOH, X= I, Br,CI

Entry	Aryl halide	Product	Time (h)	Yield <sup><i>b</i></sup> (%)	Reference <sup>-</sup>
1			8	95	S15
2	Br		10	85	S15
3		0 <sub>2</sub> N	6	95	S16
4	NO <sub>2</sub>	0 <sub>2</sub> N-	8	88	S16
5	COCH <sub>3</sub>	H <sub>3</sub> COC	10	80	S17
6	COCH3	H <sub>3</sub> COC	8	85	S17
7	OCH <sub>3</sub>	Н <sub>3</sub> СО-	12	80	S18
8	CH <sub>3</sub>	H <sub>3</sub> C	13	80	S19



R= H, -NO<sub>2</sub>, -COCH<sub>3</sub>, -CHO, -CH<sub>3</sub>, -OMe, -CN, -COOH, X= I, Br,CI





R= H, -NO<sub>2</sub>, -COCH<sub>3</sub>, -CHO, -CH<sub>3</sub>, -OMe, -CN, -COOH, X= I, Br,CI

Entry	Aryl halide	Product	Time (h)	Yield <sup>b</sup> (%)	Reference <sup>†</sup>
16			22	65	S15
17		O <sub>2</sub> N	20	68	S16
18	CI COCH3	Н3СОС-	24	60	S17
19		NC	26	68	S20

<sup>*a*</sup> Reactions were carried out using 1 mmol Aryl halide, 1.2 mmol sodium salt of phenyltrihydroxyborate, (1:5) by volume DMF : water under 90  $^{\circ}$ C refluxing condition with 0.02 g Pd-MPTAT-1 catalyst. <sup>*b*</sup> Yields refer to those purified products based on <sup>1</sup>H NMR and GC analysis (supporting information<sup>†</sup>).

resulting in the formation of C within the mesoporous polymer. Finally the reductive elimination from C regenerates A.

# **Reusability of catalyst**

After the reaction was over, the Pd-MPTAT-1 catalyst was recovered through filtration under vacuum. Recovered solid was extensively washed with water, dichloromethane, acetone, and THF, until GC analysis of the filtrate shows no detectable amounts of reagents and products. The catalyst was then dried under vacuum overnight before performing the re-usability test. The strong interaction between Pd(II) and the highly functionalized polymeric surface due to the presence of the three *N*atoms in the triazine moiety and the three allylic *O*-atoms, which strongly coordinate with the Pd centres, thereby preventing any sort of metal leaching during the catalytic reactions, rendering highly activity and selectivity of the catalyst. High catalytic activity of the Pd-catalysts in the C–C coupling reactions has been explained through the reactive centres involving N–Pd–O binding sites.<sup>37,38</sup> In Fig. 10 we have plotted the conversion levels for the Pd-MPTAT catalyst in Suzuki–Miyaura coupling reaction between iodobenzene and the sodium salt of phenyl trihydroxylborate in water–DMF. As seen from the plot that the catalyst is reusable up to sixth times and only a small decrease in the product yield from 92 to 78% occurred.

## Proof of heterogeneity of the catalyst

We have checked the heterogeneity criteria of our Pd-MPTAT-1 catalyst by the hot filtration test<sup>39</sup> with bromo benzene and the



**Fig. 9** Catalytic cycle of Suzuki-Miyaura cross-coupling reaction over Pd-MPTAT-1.



Fig. 10 Recycle efficiency of Pd-MPTAT-1 in Suzuki-Miyaura coupling reaction between iodobenzene and sodium (trihydroxyl)-phenylborate in water–DMF.

sodium salt of phenyl trihydroxyborate (Suzuki) and the solid phase poisoning test<sup>40</sup> with bromo benzene and styrene (Heck).

#### Hot filtration test

To check whether Pd is being leached out from the solid catalyst to the solution or weather the catalyst is truly heterogeneous in nature, Suzuki cross-coupling reaction between iodobenzene and phenyl trihydroxyborate has been selected for the investigation purposes. So, to serve for that purpose, 1 mmol iodobenzene and 1.2 mmol phenyl trihydroxyborate were taken in a two neck round bottom flask. Then 5:1 mixture of water and DMF (by volume) was added along with 0.02 g of Pd-MPTAT-1 catalyst maintaining 80 °C during the reaction. After continuing the reaction for about 4 h, catalyst was separated by filtration and the filtrate was then analyzed by a GC to check the conversion values which was found to be 25%. The filtrate was then continued to reflux for another 6 h without any catalyst. After completion of 14 h, GC analysis revealed no increase in conversion values (25%) in absence of catalyst. This result suggested that the coupling reaction cannot proceed after removal of the catalyst or the catalyst is truly heterogeneous in nature because no evidence of leaching of the palladium from solid support was observed as confirmed from atomic absorption spectroscopic (AAS) measurement of the hot filtrate solution. Further, during the course of those reactions no evidence for the decomposition of the polymeric solid support was observed. All these results clearly demonstrate that surface bound Pd remained intact within the solid framework and even a trace amount of Pd was not leached out from the solid catalyst to the solution. Thus our novel polymeric Pd-support is an outstanding heterogeneous catalyst for several C–C cross-coupling reactions in the presence of water.

#### Solid phase poisoning test

Further the heterogeneous nature of the catalyst was checked by employing a solid-phase poisoning test, where we have used 3-mercaptopropyl-functionalized silica (commercially available) as an efficient Pd scavenger. In a typical experimental procedure, iodobenzene (1 mmol), styrene (1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol), water (10 ml) and ethanol (5 ml) were mixed in a round bottom flask along with 0.02 g Pd-MPTAT-1 catalyst and 0.05 g 3mercaptopropyl-functionalized silica. The whole mixture was refluxed in an oil bath for about 12 h at 110 °C. No change in conversion was observed vis-à-vis our previous experiment (Table 1, entry 1, yield 95% in both cases), which clearly demonstrates that our novel catalyst is heterogeneous in nature. Since –SH functionalized mesoporous silica forms a complex with the leached palladium, it can deactivate the catalyst otherwise. Thus, we may conclude that there is no question of palladium leaching from Pd-MPTAT-1 to the solution during a Heck coupling reaction.

# Conclusions

In summary, we have successfully synthesized a novel organic mesoporous polymer through facile and simple polymerization of 2,4,6-triallyloxy-1,3,5-triazine using APS as radical initiator and SDS as the template under acidic pH conditions. TEM image analysis suggests the presence of 2D hexagonal mesopores throughout the polymer. The template free polymer when anchored with Pd(II) shows high catalytic activity in several C-C cross-coupling reactions like Heck, Sonogashira and Suzuki-Miyaura under eco-friendly conditions without using phosphine containing catalyst or environmentally hazardous solvents. Under certain circumstances chloroarenes also responded to coupling reactions to some extent in the presence of this catalyst. Aryl chlorides normally remain inactive under cross-coupling conditions and there are a very few catalysts available which can activate chloro-compounds<sup>34</sup> as well. Pd-MPTAT-1 is very active in the presence of water, which is a green solvent and can be recycled several times without much loss in reactivity. Thus this C-C cross-coupling reactions presented herein could be a versatile tool for the production of several value added organics in a green chemical route.

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