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Pd Nanoparticles Immobilized on Nanosilica Triazine Dendritic Polymer: A Reusable Catalyst for the Synthesis of Mono-, Di-, and Trialkynylaromatics by Sonogashira Cross-Coupling in Water

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Palladium nanoparticles immobilized on nano-silica triazine dendritic polymer (Pd_{np} -nSTDP) was found to be a highly effective catalyst for the Sonogashira cross-coupling of aryl halides (iodides, bromides, and chlorides) with aromatic and aliphatic terminal alkynes. This reaction was best performed in water as a green solvent in the presence of just 0.01 mol-% of the catalyst at room temperature. Efficient synthesis of

V- and star-shaped polyalkynylated molecules with a benzene, pyridine, or pyrimidine central core was also achieved through Sonogashira cross-coupling of dihalo and trihalo aromatics with terminal alkynes in the presence of this catalytic system. The Pd_{np} -nSTDP catalyst was easily recovered and reused several times without significant loss of reactivity.

Introduction

The Sonogashira cross-coupling reaction between a terminal alkyne and an aryl or vinyl halide represents a valuable and facile synthetic strategy for the formation of a new $C(sp)-C(sp^2)$ bond.^[1] This reaction has been widely used in the synthesis of natural products^[2] and biologically active molecules,^[3] as well as in materials science.^[4] Traditionally, the Sonogashira reaction is carried out in the presence of homogeneous palladium catalysts such as Pd(PPh₃)₄, Pd(OAc)₂, PdCl₂(PPh₃)₂, and PdCl₂(CH₃CN)₂.^[5] In spite of their great utility, these homogeneous catalysts suffer from disadvantages such as difficulties in separation and recovery, sensitivity to air, and the formation of alkyne homocoupling products (Glaser coupling).^[6] Furthermore, contamination of the desired product with palladium limits the applicability of these homogeneous catalysts in large scale operations, and can lead to serious environmental, economic, and safety problems, especially in the pharmaceutical industry.^[7] In order to overcome these problems and to improve the environmental and economical sustainability of the Sonogashira reaction, many heterogeneous palladiumbased catalytic systems have been developed.^[8,9] However, high temperatures, long reaction times, and the use of large amounts of palladium and organic solvents are limitations

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and drawbacks of many of the previously reported methods. Despite the enormous number of publications, the development of efficient and greener protocols for the Sonogashira cross-coupling reaction is still challenging and still desirable.

Since a large amount of waste in the environment is attributed to the use of organic solvents,^[10] there is growing demand for improvement of organic reactions in environmentally-friendly media.^[11] During recent years, water has gained special attention as a reaction medium for organic synthesis, as it is nontoxic, nonflammable, cheap, and environmentally benign.^[12] Moreover, the chemical and physical properties of water can lead to selectivity and/or reactivity that cannot be attained in organic solvents.^[13] Therefore, the introduction of highly efficient and green protocols using recoverable catalysts in water as the reaction medium may be seen as a worthwhile goal.

In recent years, dendritic polymers have attracted significant attention, due to their applications in different areas such as drug delivery,^[14] medicinal chemistry,^[15] collar cells,^[16] and nanoscience.^[17] A characteristic feature of dendritic polymers is the presence of internal cavities. These cavities enable the polymers to act as molecular boxes for the encapsulation of organic molecules, ions, or metal nanoparticles. Such metal-containing dendritic polymers are recognized to catalyse various organic reactions.^[18] Moreover, the immobilization of these metal-encapsulated dendritic catalysts on solid supports makes them easily recoverable and reusable, which is very important from economical and environmental points of view.^[19]

Recently, we reported the palladium nanoparticles immobilized on nano-silica triazine dendritic polymer

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Scheme 1. Sonogashira cross-coupling catalysed by Pd_{nn} -nSTDP.

(Pd_{nn}-nSTDP) (Figure 1) as an efficient and reusable catalyst for Suzuki-Miyaura cross-coupling and Heck reactions,^[20a] and C-S cross-coupling reactions.^[20b] In a continuation of our work on new applications of the Pd_{nn}-nSTDP catalytic system, and also on the development of useful synthetic methodologies,^[21] in this paper, we report an efficient method for synthesis of mono-, di-, and trialkynylaromatic and heteroaromatic compounds by Sonogashira cross-coupling of aryl halides with terminal alkynes catalysed by Pd_{np}-nSTDP in water as a green reaction medium (Scheme 1).



Figure 1. The structure of the Pd_{np} -nSTDP catalyst.

Results and Discussion

Sonogashira Cross-Coupling of Aryl Halides with Terminal Alkynes Catalysed by Pd_{np}-nSTDP

To find the optimal reaction conditions, we examined the Sonogashira cross-coupling between bromobenzene (1 mmol) and phenylacetylene (1.1 mmol) in the presence of the Pd_{nn} -nSTDP catalyst as a model reaction (Table 1). First, a wide range of bases including NaOH, Na₂CO₃, K₂CO₃, NEt₃, tBuNH₂, piperidine, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and DIPEA (N,N-diisopropylethylamine) were screened, and we found that DIPEA was the most effective base both in terms of reaction time and yield. To study the effect of the solvent, the model reaction was carried out in the presence of Pd_{np}-nSTDP/DIPEA in various solvents (500 μ L), including H₂O, DMF, THF, EtOH, H₂O/DMF (1:1), and H₂O/EtOH (1:1), and also under solvent-free conditions at room temperature. The highest yield and the shortest reaction time were obtained in H₂O. Finally, the effect of the catalyst loading on the yield of the desired product in model reaction was investigated,

Table 1. Optimization of conditions for the Sonogashira cross-coupling of bromobenzene with phenylacetylene catalysed by Pd_{np} nSTDP.[a]



Entry	Base	Catalyst Solvent [mol-% Pd]		Time [h]	Yield [%] ^[b]
1	NaOH	0.01	H ₂ O	10	12
2	Na ₂ CO ₃	0.01	H_2O	10	34
3	K_2CO_3	0.01	H_2O	10	35
4	Et ₃ N	0.01	H_2O	8	86
5	tBuNH ₂	0.01	H_2O	8	80
6	piperidine	0.01	H_2O	7	65
7	DBU	0.01	H_2O	8	50
8	DIPEA	0.01	H_2O	5	95
9	DIPEA	0.01	_	5	29
10	DIPEA	0.01	H ₂ O/DMF (1:1)	6	90
11	DIPEA	0.01	H ₂ O/EtOH (1:1)	6	71
12	DIPEA	0.01	DMF	6	78
13	DIPEA	0.01	THF	8	49
14	DIPEA	0.01	EtOH	6	60
15	DIPEA	0.012	H_2O	5	95
16	DIPEA	0.008	H_2O	10	65
17	DIPEA	0.006	H ₂ O	10	61

[a] Reaction conditions: bromobenzene (1 mmol), phenylacetylene (1.1 mmol), base (1 mmol), Pd_{np}-nSTDP, solvent (500 µL), room temperature. [b] Isolated yield.

and the highest yield was obtained using 0.01 mol-% of the palladium catalyst. Consequently, from the observations summarized in Table 1, we conclude that 0.01 mol-% of the catalyst, DIPEA (1 mmol) as the base, in H₂O (500 μ L) at room temperature, are the most appropriate reaction conditions for this transformation (Table 1). It is important to mention that the amount of H₂O has an effect on the product yield. When the experiments were carried out in 1 mL and 2 mL of H₂O, the desired product was obtained in 88 and 85% yields, respectively, and a small amount of the homocoupling product was detected.

Under these optimized reaction conditions, various aryl iodides and bromides were cross-coupled with aromatic and aliphatic terminal alkynes in the presence of Pd_{np}-nSTDP/ DIPEA in H₂O at room temperature to give the desired products in high yields (Table 2, entries 1-11). Impressed with the results with aryl iodides and bromides, we tried to further expand the scope of Pd_{np}-nSTDP catalyst in coupling reactions using aryl chlorides, which are less reactive but cheaper and more readily available than aryl iodides and bromides. The Sonogashira cross-coupling of activated and deactivated aryl chlorides with terminal alkynes proceeded effectively to give the corresponding products in 87-90% yields (Table 2, entries 12–14) under the same conditions, but these reactions required longer times. It is interesting to note that this method is better than the many previously reported Sonogashira cross-coupling methods in terms of reaction times, reaction temperatures, and/or the amount of the catalyst.^[22]

Table 2. Sonogashira cross-coupling of aryl halides with aromatic or aliphatic alkynes catalysed by Pd_{np} -nSTDP^[a]

F		-X + 📰 -	$R^{2} \xrightarrow[H_{2}]{Pd_{np}\text{-}nSTDP} (0.01 \text{ mol-\%}) \\ \hline DIPEA (1 \text{ mmol}) \\ H_{2}O (500 \mu\text{L}) \\ r.t.$	R	<u></u>
Entry	Х	\mathbb{R}^1	\mathbb{R}^2	Time [h]	Yield [%] ^[b]
1	Ι	Н	Ph	2	96
2	Ι	2-Me	Ph	2	93
3	Ι	4-MeO	Ph	2	95
4	Ι	4-MeO	<i>n</i> -butyl	2	85
5	Ι	4-MeO	$4-ClC_6H_4$	2	95
6	Br	Н	Ph	5	95
7	Br	4-MeO	Ph	5	92
8	Br	Ac	Ph	5	94
9	Br	Ac	$4-ClC_6H_4$	5	95
10	Br	Ac	<i>n</i> -butyl	5	80
11	Br	Н	pentyl	5	84
12	C1	Н	Ph	10	87
13	C1	Ac	3-MeOC ₆ H ₄	10	90
14	Cl	4-MeO	Ph	10	90

[a] Reaction conditions: aryl halides (1 mmol), aryl acetylene (1.1 mmol), DIPEA (1 mmol), Pd_{np} -nSTDP (0.01 mol-% Pd), H_2O (500 µL), room temperature. [b] Isolated yield.

Synthesis of V- and Star-Shaped Molecules Catalysed by Pd_{np}-nSTDP

Highly conjugated polyalkynylated organic molecules are of significant interest due to their extensive applications in a wide range of electronic and optoelectronic devices.^[23–25] These compounds are suitable candidates for applications as liquid crystals,^[26] non-linear optical materials,^[27] light-emitting materials,^[28] and building blocks for two-dimensional carbon networks.^[23a,29] In addition, some of them have been used as core structures for dendritic materials^[30] and functional dyes.^[31] Thus, the development of new and highly efficient protocols for their preparation is of practical importance and highly desirable.

Encouraged by the excellent results described above for the Sonogashira cross-coupling of aryl halides with terminal alkynes, we went on to investigate the synthetic potential of the Pd_{np}-nSTDP catalytic system for the synthesis of V- and star-shaped molecules. The results are shown in Table 3. The Sonogashira cross-coupling of 2,6-dibromopyridine with phenylacetylene, 4-chlorophenylacetylene, and/or 3-methoxyphenylacetylene proceeded smoothly in the presence of Pd_{np}-nSTDP and DIPEA in H₂O at room temperature to give the desired dialkynylated V-shaped molecules in 91-95% yields (Table 3, P1-P3). Under these conditions, trialkynylated star-shaped molecules were also obtained in high yields (85-92%) by Sonogashira cross-coupling of 1,3,5-tribromobenzene or 2,4,6-trichloropyrimidine with phenylacetylene and/or 3-methoxyphenylacetylene (Table 3, **P4–P7**).

It is also important to note that the synthesis of trialkynylated star-shaped molecules can be achieved directly from 4-haloacetophenones by Sonogashira cross-coupling and subsequent cyclotrimerization reactions. As shown in Scheme 2, the Sonogashira reactions of 4-bromoacetophenone with phenylacetylene, 4-bromoacetophenone with 4chlorophenylacetylene, and 4-chloroacetophenone with 3methoxyphenylacetylene, gave the desired cross-coupled products, which, upon cyclotrimerization in the presence of $H_3PW_{12}O_{40}$ (HPW),^[32] gave the corresponding star-shaped molecules (**P8–P10**) in high yields (Scheme 2).

In Table 4, the result for the coupling of iodobenzene with phenylacetylene by this method is compared with some results from the literature with several Pd catalysts in copper-free Sonogashira reactions. Compared to most of the previously reported methods, the yield with the Pd_{np} -nSTDP catalyst is higher, the reaction time is shorter, and the reaction temperature is lower. Moreover, the amount of the Pd_{np} -nSTDP catalyst required is much lower, and the turnover frequency (TOF) is higher, indicating the efficiency of this method.

We carried out a recycling investigation of the catalyst in the reaction of bromobenzene with phenylacetylene under the optimized conditions. After completion of the reaction, ethyl acetate (15 mL) was added, and the catalyst was separated by centrifugation, dried, and reused for eight consecutive trials without any appreciable loss in activity (Table 5). After that, the activity of the catalyst decreased slightly, and the desired product was obtained in 84 and 80% yields in the ninth and tenth recycles, respectively. Furthermore, palladium leaching from the Pd_{np}-nSTDP catalyst was determined, and ICP analysis of the ethyl acetate solution showed that the Pd content of the solution was less than 0.10 ppm. **FULL PAPER**

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Entry	Substrate	Alkyne	Product	Time (h)	Yield (%) ^[a]
1 ^[b]	Br		P1	5	95
2 ^[b]	Br	[™] C) _{Cl}		5	91
3 ^[b]	Br	OMe	P3 OMe OMe	5	95
4 ^[c]	Br Br		P4	8	92
5 ^[0]	Br Br	OMe	MeO P5 OMe	8	86
6 ^[c]		Q.		8	88
7 ^[c]		OMe	MeQ P7	8	85

Table 3. Synthesis of V- and star-shaped molecules by Sonogashira cross-coupling catalysed by Pd_{np}-nSTDP.

[a] Isolated yield. [b] Reaction conditions: 2,6-dibromopyridine (1 mmol), arylacetylene (2.2 mmol), DIPEA (2 mmol), Pd_{np}-nSTDP (0.02 mol-% Pd), H₂O (1 mL), room temperature. [c] Reaction conditions: 1,3,5-tribromobenzene or 2,4,6-trichloropyrimidine (1 mmol), arylacetylene (3.3 mmol), DIPEA (3 mmol), Pd_{np}-nSTDP (0.03 mol-% Pd), H₂O (1 mL), room temperature.

Table 4.	Comparison	of the	results of	' Sonogashira	coupling	reactions	catalysed	by P	d _{np} -nSTDP	and	reported	results	with s	some o	other	Pd
catalysts.																

		$+$ \longrightarrow Cat			
Entry	Catalyst	Condition	Time [h] (Yield [%] ^[a])	TOF [h ⁻¹]	Ref.
1	Pd _{np} -nSTDP (0.01 mol-%)	DIPEA, H ₂ O, r.t.	2 (96)	4800	this work
2	DAB dendr/Pd(OAc) ₂ , $G2^{[b]}$ (1 mol-%)	Et ₃ N, N ₂ , 25 °C	40 (100)	2.5	[33a]
3	$PNP-SSS^{[c]}$ (1.2 mol-%)	K_2CO_3 , H_2O_3 , reflux	3 (95)	26.4	[33b]
4	$Pd^{0}-Mont.^{[d]}$ (0.07 mol-%)	CH ₃ CN, Et ₃ N, 82 °C	3 (90)	428	[33c]
5	Silica–Pd ^[e] (1 mol-%)	Piperidine, 70 °C	0.16 (92)	575	[33d]
6	Polymer NHC-Pd complex (1 mol-%) ^[f]	Cs ₂ CO ₃ , 60 °C	3 (85)	28.3	[33e]

[a] Isolated yield. [b] Diaminobutane dendrimer/Pd(OAc)₂. [c] Immobilization of Pd nanoparticles on a silica-starch substrate. [d] Pd^0 nanoparticles into the nanopores of modified Montmorillonite. [e] Silica-supported palladium. [f] NHC = N-heterocyclic carbene.

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Sonogashira Cross-Coupling in Water



Scheme 2. Synthesis of star-shaped molecules from 4-haloacetophenones.

Table 5. The recycling of Pd_{np} -nSTDP in the Sonogashira crosscoupling of bromobenzene with phenylacetylene.^[a]

Cycle	1	2	3	4	5	6	7	8	9	10
Yield [%] ^[b]	95	93	94	94	92	92	91	90	84	80

[a] Reaction conditions: bromobenzene (1 mmol), phenylacetylene (1.1 mmol), DIPEA (1 mmol), Pd_{np}-nSTDP (0.01 mol-% Pd), H₂O (500 µL), room temperature, 5 h. [b] Isolated yield.

Conclusions

In conclusion, we have developed an environmentally friendly and efficient method for the Sonogashira crosscoupling of aryl halides (iodides, bromides, and chlorides) with aromatic and aliphatic terminal alkynes. The method uses palladium nanoparticles immobilized on nano-silica triazine dendritic polymer (Pd_{np}-nSTDP) as a catalyst, and the reactions are run in the greenest solvent, water. This catalytic system can also be used efficiently for the synthesis of V- and star-shaped molecules. The catalyst can be recovered and reused, the experimental procedure is simple and green, and the yields are high, all of which combine to make this method a valid alternative to existing reaction protocols for the preparation of these fine chemicals.

Experimental Section

General Remarks: Chemicals were purchased from Fluka and Merck. Melting points was determined with a Stuart Scientific SMP2 apparatus. FTIR spectra were recorded with a Nicolet-Impact 400D spectrophotometer. ¹H and ¹³C NMR spectra (400 and 100 MHz) were recorded with a Bruker Avance 400 MHz spectrometer using CDCl₃ solvent. Elemental analysis was carried out

with a LECO CHNS-932 instrument. The Pd content of the catalyst was determined by Jarrell-Ash 1100 ICP analysis. The Pd_{np} -nSTDP catalyst was prepared according to our previously reported method.^[20a]

General Procedure for the Sonogashira Cross-Coupling of Aryl Halides with Terminal Alkynes Catalysed by Pd_{np} -nSTDP: A mixture of aryl halide (1 mmol), terminal alkyne (1.1 mmol), DIPEA (1 mmol), and Pd_{np} -nSTDP (0.01 mol-% Pd) in H₂O (500 µL) was stirred at room temperature for the time indicated in Table 2. The progress of the reaction was monitored by TLC (diethyl ether/ethyl acetate, 6:1). After the reaction was complete, ethyl acetate (15 mL) was added, and the catalyst was separated by centrifugation. The organic phase was washed with H₂O (2 × 10 mL), and dried with anhydrous MgSO₄, and the solvents were evaporated. The residue was recrystallized from ether and ethyl acetate (3:1) to give the pure product (Table 2).

General Procedure for Synthesis of V- and Star-Shaped Molecules by Sonogashira Cross-Coupling Catalysed by Pd_{np} -nSTDP: A mixture of 2,6-dibromopyridine, 1,3,5-tribromobenzene or 2,4,6-trichloropyrimidine (1 mmol), terminal alkyne (2.2–3.3 mmol), DIPEA (2–3 mmol), and Pd_{np} -nSTDP (0.02–0.03 mol-% Pd) in H₂O (1 mL) was stirred at room temperature for the time indicated in Table 3. The progress of the reaction was monitored by TLC (diethyl ether/ethyl acetate, 6:1). After the reaction was complete, ethyl acetate (15 mL) was added, and the catalyst was separated by centrifugation. The organic layer was washed with water (2× 10 mL), and dried with anhydrous MgSO₄. Evaporation of the solvent followed by recrystallization of the crude product from ether and ethyl acetate (1:1) gave the pure product (Table 3).

Synthesis of P8, P9, and P10 by Sonogashira Cross-Coupling and Subsequent Cyclotrimerization: The synthesis was carried out in two steps (Scheme 2). First, the reaction of the 4-haloacetophenone with the terminal alkyne was carried out according to the general procedure given above for Sonogashira cross-coupling in the presence of Pd_{np} -nSTDP (Table 2, entries 8, 9, and 13). This gave the

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corresponding 4-(arylethynyl)acetophenone. Then, the cyclotrimerization of the 4-(arylethynyl)acetophenone was carried out according to our previously reported procedure.^[32] Thus, a mixture of 4-(arylethynyl)acetophenone (1 mmol) and $H_3PW_{12}O_{40}$ (15 mol-%) was exposed to microwave irradiation (450 W, 90 °C) for 20 min. The progress of the reaction was monitored by TLC (diethyl ether/ ethyl acetate, 6:1). After the reaction was complete, hot ethyl acetate (10 mL) was added, and the catalyst was separated by filtration. Evaporation of the solvent followed by recrystalization of the crude material from ethyl acetate gave the pure product.

Supporting Information (see footnote on the first page of this article): Experimental details and copies of the ¹H and ¹³C NMR spectra of all compounds.

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FULL PAPER

Palladium Nanoparticles

Palladium nanoparticles immobilized on nano-silica triazine dendritic polymer (Pd_{np} -nSTDP) was found to be a highly effective catalyst for the Sonogashira cross-coupling of aryl halides (iodides, bromides, and chlorides) with aromatic and aliphatic terminal alkynes. The reaction was best performed in water as a green solvent in the presence of just 0.01 mol-% of the catalyst at room temperature.



Pd Nanoparticles Immobilized on Nanosilica Triazine Dendritic Polymer: A Reusable Catalyst for the Synthesis of Mono-, Di-, and Trialkynylaromatics by Sonogashira Cross-Coupling in Water

Keywords: Heterogeneous catalysis / Water chemistry / Palladium / Nanoparticles / Cross-coupling / Dendrimers / Alkynes

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