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Palladium nanoparticles immobilized on a nano-silica triazine dendritic polymer: a recyclable and sustainable nanoreactor for C–S cross-coupling†

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Dendrimers are of great interest due to their special structural topology and chemical versatility. Owing to their properties, dendrimers have found practical applications in catalytic processes as efficient nanoreactors. Therefore, we herein report an environmentally attractive strategy and highly efficient route for the synthesis of a wide variety of diaryl sulfides using palladium nanoparticles immobilized on a nano-silica triazine dendritic polymer (Pd_{np}-nSTDP) as a nanoreactor. In this manner, different diaryl or aryl heteroaryl sulfides and bis(aryl/heteroarylthio)benzene/anthracene/pyridine derivatives were prepared *via* C–S cross-coupling reactions of aryl halides with diaryl/diheteroaryl disulfides under thermal conditions and microwave irradiation. The catalyst could be easily recovered and reused several times without any significant loss of its activity.

Introduction

Over the last few years, chemists have tried to understand the principles and significance of nanoscale reaction systems. Since the introduction of the concept of supramolecular nanoreactors by Breslow,[1] nanoreactors have been investigated increasingly in the field of catalysis.[2] The most significant supramolecular nanoreactors that have been established so far for the stabilization of catalytically active nanoparticles are cucurbiturils, porphyrins, metal–organic frameworks, micelles, colloidosomes and dendrimers.[3–9] Along this line, dendrimers, which are highly branched and tree-like macromolecules with 3D structures, chemical functionalities and internal cavities, can act as excellent hosts for encapsulation of a variety of metal ions, complexes and nanoparticles.[10–15]

Diarylsulfides are important intermediates in a wide variety of organic synthesis and play a significant role in many biologically and pharmaceutically active compounds.[16] These moieties are used for treatment of inflammation,[17] cancer,[18,19] immunodeficiency virus (HIV),[17] and Alzheimer's and Parkinson's diseases.[20] Because of their importance and useful properties, different approaches have been developed for the synthesis of diarylsulfides *via* C–S cross-coupling reactions.[21,22] Generally, in these coupling reactions, thiols (ArSH) are reacted with aryl halides or aryl boronic acids as aryl donors in the presence of different catalytic systems including Fe,[23–25] Cu,[26–28] Ni,[29,30] Co,[31,32] In (ref. 33) and Pd.[34–38]

However, thiols have offensive odors and are easily oxidized to the corresponding diaryl disulfides (ArSSAr) in air. Thus, diaryl disulfides are often produced as a by-product in the above mentioned methods.[39] To solve this problem and for the effective conversion of thiols to diaryl sulfides, aryl donors are usually used in excess.[40] On the contrary, diaryl disulfides are air stable, and easy to handle. Nevertheless, little attention has been paid to the cross-coupling of diaryl disulfides as sulfur nucleophile with aryl donors.[41–45] Accordingly, development of convenient methods and catalysts for the synthesis of diaryl sulfides *via* such a cross-coupling reactions is still critically needed.

Based on the green chemistry concept and principal, synthetic approach and process should be premeditated to use and generate substances which exhibit little or no hazard to human body and the natural environment. Moreover, these chemical transformations are often performed with high yields, at low temperatures, in short reaction times, and in the presence of low amount of the catalyst in water or aqueous media.[46]

Nano-silica triazine dendritic polymer (nSTDP) can be effectively applied for nanoscale organic transformations. During the course of our research on the application of this nanoreactors[47–50] and also our interest in Pd-catalyzed coupling reactions, herein we disclose a convenient method for mono- and di C–S cross-coupling reactions with diaryl or diheteroaryl disulfides using Pd_{np}-nSTDP (Fig. 1) as an eco-friendly nanoreactor under conventional heating and microwave irradiation (Scheme 1). As far as we know, the use of palladium nanoparticles-based dendritic catalyst for such a coupling

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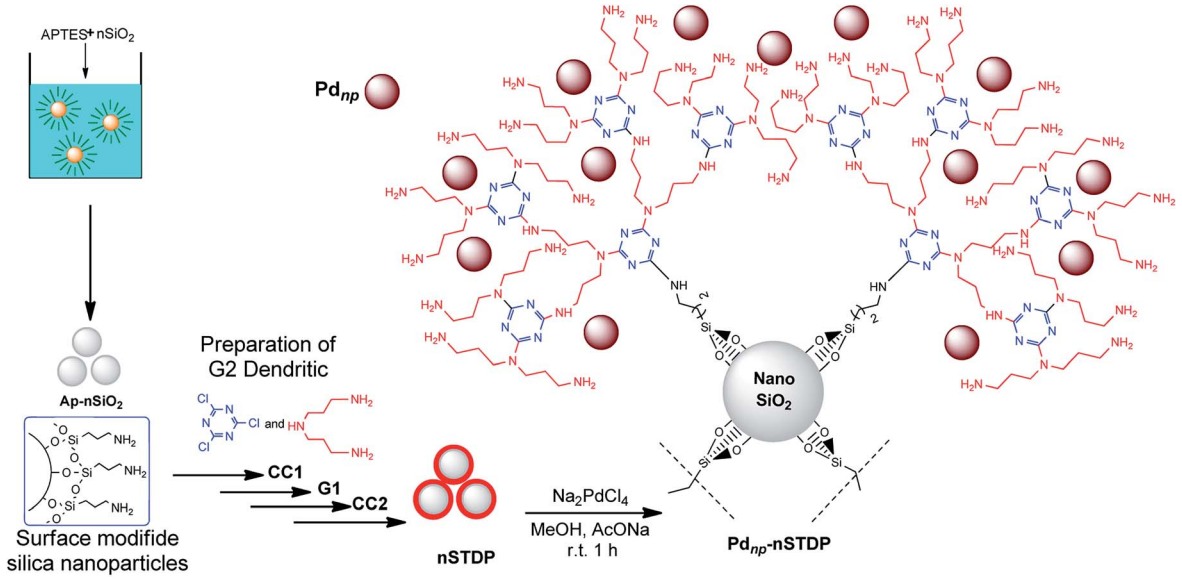
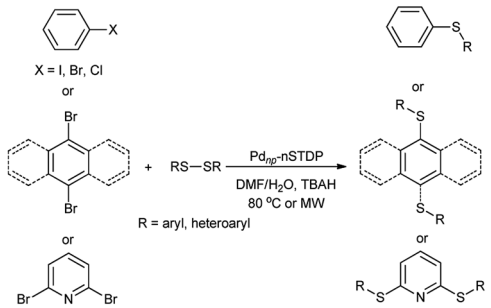


Fig. 1 Schematic illustration of preparation of palladium nanoparticles immobilized on nano silica triazine dendritic polymer (Pd_{np}-nSTDP) catalyst.



Scheme 1 C–S cross-coupling catalyzed by Pd_{np}-nSTDP.

reactions is reported for the first time and could be considered as an exclusive feature of nanoscience and green chemistry.

Results and discussion

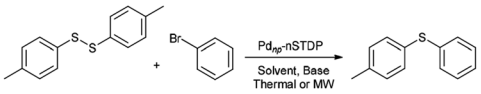
Fig. 1 illustrates the synthetic pathway of palladium nanoparticles immobilized on nano silica triazine dendritic polymer (Pd_{np}-nSTDP).[47] Initially, nano-silica was functionalized with 3-aminopropyltrimethoxysilane (APTES) to afford aminopropyl-functionalized nano-silica (AP-$nSiO_2$). Then, treatment of AP-$nSiO_2$ with cyanuric chloride (CC) in the presence of diisopropylethylamine (DIPEA) at room temperature afforded CC1-$nSiO_2$ which upon reaction with bis(3-aminopropyl)amine gave G1. After that, the reaction of G1 with cyanuric chloride (CC) and DIPEA provided CC2-$nSiO_2$ which in turn was transformed to G2 (nSTDP) by the reaction with bis(3-aminopropyl)amine. Finally, the Pd_{np}-nSTDP catalyst was prepared by reduction of $Na_2Pd_2Cl_6$ (prepared *in situ* from $PdCl_2$ and NaCl)[51] in methanol and sodium acetate at 60 °C in the presence of nSTDP (ESI†). The palladium loading of the catalyst was measured by ICP analysis and it was found that the amount of Pd in the catalyst is 1.27% (0.12 mmol g^{-1} of nSTDP).

Initially, for screening experiments, the coupling reaction of 4-bromoanisole (1 mmol) with di-*p*-tolyl disulfide (0.5 mmol) was carried out using Pd_{np}-nSTDP catalyst for determination of effective factors such as types of base and solvent, temperature, catalyst loading and MW power. The results are shown in Table 1. Primarily, different bases such as NEt_3, piperidine, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), NaOH, Na_2CO_3, K_2CO_3 and 20% solution of tetrabutylammonium hydroxide in water (TBAH) were examined. Amongst, TBAH was found as the most effective base in terms of both reaction time and yield. The effect of solvent was also checked in the model reaction and highest yield was obtained in a 1 : 1 mixture of H_2O–DMF (Table 1, entries 7–12). Next, we investigated the catalyst loading (0.08–0.12 mol% Pd) and 0.1 mol% (8 mg) of the catalyst was found to be the optimum amount for completion of this reaction (Table 1, entries 7, 13 and 14). Finally, the effect of temperature on the activity of this catalyst was studied in the range of 70 to 100 °C. As can be seen in Table 1, by increasing the temperature to 80 °C, the yield of the reaction was improved but its increasing from 80 to 100 °C did not influence the yield of the product. Therefore, 0.1 mol% (8 mg) of the catalyst and TBAH base in a mixture of H_2O–DMF (1 : 1) at 80 °C are the most appropriate reaction conditions for this transformation (Table 1, entry 7). It is worth mentioning that aqueous DMF has been used as a green solvent in different organic transformations, especially in cross coupling reactions.[52]

In order to evaluate the effect of microwave irradiation (MW) on this transformation, the model reaction was carried out under MW at different conditions (Table 1, entries 17–21). The highest yield was obtained with an applied power of 230 W at 80 °C (Table 1, entry 19).

The scope and generality of this protocol were then investigated in the C–S cross-coupling of various aryl halides with different diaryl disulfides (Table 2). The reaction of a series of

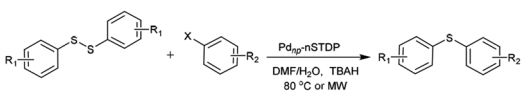
Table 1 Optimization of the C–S cross-coupling of 4-bromoanisole with di-*p*-tolyl disulfide catalyzed by Pd_{np}-nSTDP[a]



Entry	Base	Catalyst (mol% Pd)	Solvent[a]	Method	Time (h)	Yield[b] (%)	TON[c]	TOF[d] (h^{-1})
1	Et_3N	0.1	DMF	80 °C	24	15	150	6.25
2	Piperidine	0.1	DMF	80 °C	24	40	400	16.7
3	DBU[e]	0.1	DMF	80 °C	24	28	280	11.7
4	NaOH	0.1	DMF	80 °C	12	64	640	53.3
5	K_2CO_3	0.1	DMF	80 °C	12	60	600	50.0
6	Na_2CO_3	0.1	DMF	80 °C	12	83	830	69.2
7	TBAH[f]	0.1	H_2O/DMF	80 °C	5	95	950	190.0
8	TBAH	0.1	H_2O/EtOH	75 °C	12	51	510	42.5
9	TBAH	0.1	H_2O/DMSO	80 °C	12	86	860	71.7
10	TBAH	0.1	H_2O/dioxane	80 °C	12	85	850	70.8
11	TBAH	0.1	H_2O/toluene	80 °C	12	30	300	25.0
12	TBAH	0.1	—	80 °C	12	45	450	37.5
13	TBAH	0.08	H_2O/DMF	80 °C	5	53	625	125.0
14	TBAH	0.12	H_2O/DMF	80 °C	5	95	792	158.3
15	TBAH	0.1	H_2O/DMF	100 °C	5	95	950	190.0
16	TBAH	0.1	H_2O/DMF	70 °C	8	74	740	92.5
17	TBAH	0.1	H_2O/DMF	170 W, 50 °C	15 min	85	850	226.6
18	TBAH	0.1	H_2O/DMF	200 W, 70 °C	10 min	90	900	5400
19	TBAH	0.1	H_2O/DMF	230 W, 80 °C	10 min	95	950	5700
20	TBAH	0.15	H_2O/DMF	230 W, 80 °C	10 min	73	487	2920
21	TBAH	0.08	H_2O/DMF	230 W, 80 °C	10 min	62	775	4650

[a] The reaction was performed using 1 mL of solvent and 1 mmol of base. [b] Isolated yield. [c] TON = turnover numbers. [d] TOF = turnover frequency. [e] DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. [f] TBAH = 20% tetrabutylammonium hydroxide in water.

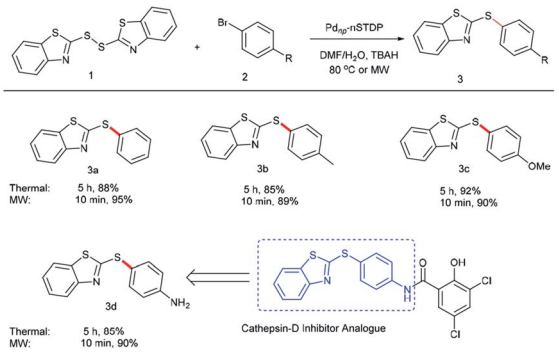
Table 2 C–S cross-coupling of aryl halides with diaryl disulfides catalyzed by Pd_{np}-nSTDP[a]



				Thermal		MW	
Entry	R^1	X	R^2	Time (h)	Yield[b] (%)	Time (min)	Yield[b] (%)
1	4-Me	I	H	3	96	5	95
2	4-Me	I	4-Me	3	94	5	95
3	4-OMe	I	4-Me	3	96	5	96
4	4-Me	I	4-Ac	3	95	5	96
5	H	I	4-Me	3	93	5	95
6	4-Me	Br	4-Ac	5	95	10	92
7	4-Me	Br	H	5	95	10	93
8	H	Br	4-Me	5	94	10	89
9	3-OMe	Br	4-OMe	5	96	10	93
10	4-Me	Br	4-OMe	5	95	10	95
11	4-Me	Br	4-CHO	5	95	10	90
12	4-Me	Cl	2-Me	10	85	25	82
13	4-Me	Cl	4-CHO	10	90	25	86
14	4-Me	Cl	4-Ac	10	87	25	90
15	4-Me	Cl	H	10	83	25	85

[a] Reaction conditions: aryl halide (1 mmol), diaryl disulfide (0.5 mmol), TBAH (1 mmol), Pd_{np}-nSTDP (0.1 mol% Pd, 8 mg), H_2O/DMF (1 : 1, 1 mL), 80 °C or MW (230 W, 80 °C). [b] Isolated yield.

Table 3 C–S cross-coupling of arylbromides and 2,2′-dithiobis(benzothiazole) catalyzed by Pd_{np}-nSTDP[a,b]



[a] Reaction conditions: aryl bromide (1 mmol), 2,2′-dithiobisbenzothiazole (0.5 mmol), TBAH (1 mmol), Pd_{np}-nSTDP (0.1 mol% Pd, 8 mg), H_2O/DMF (1 : 1, 1 mL), 80 °C or MW (230 W, 80 °C). [b] Isolated yield.

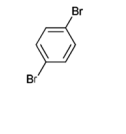
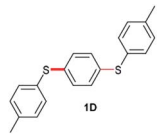
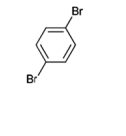
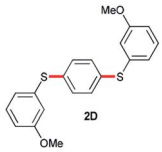
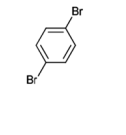
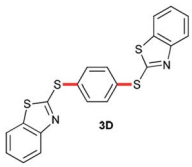
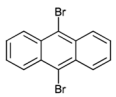
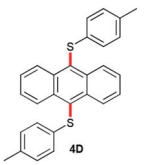
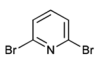
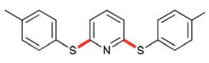
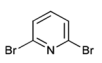
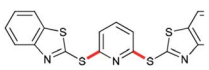
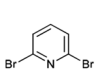
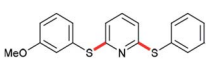
aryl iodides and bromides with different diaryl disulfides proceeded effectively in the presence of Pd_{np}-nSTDP catalyst under the optimized conditions and the desired diaryl sulfides were produced in 93–96% yields (Table 2, entries 1–11).

The applicability of this palladium-catalyzed C–S cross-coupling reactions was also examined using the less reactive but cheaper and more readily available aryl chlorides instead of their bromide and iodide counterparts. As the data revealed, the cross-coupling of aryl chlorides with diaryl disulfides proceeded smoothly in the presence of Pd_{np}-nSTDP to afford the corresponding products in 83–90% yields (Table 2, entries 12–15). The results in Table 2 disclose that the dendritic polymer accelerates the C–S cross coupling reactions due to its cavities that isolate the catalytic active sites from the surrounding environment and provide an efficient nanoreactors.

The C–S cross-coupling of these aryl halides with diaryl disulfide was also investigated under microwave irradiation, in which the desired products were provided in 82–96% yields within 5–25 min (Table 2). These results clearly showed that microwave irradiation as an eco-friendly technology has the evident advantage of very short reaction times over the conventional heating mode.

2-(Arylthio)-1,3-benzothiazoles are essential building blocks which are found in a large number of biologically and pharmaceutically active molecules.[53,54] Accordingly, we decided to explore the potential of this catalytic system in the synthesis of 2-(arylthio)-1,3-benzothiazoles *via* C–S cross-coupling of arylbromides with 2,2′-dithiobis(benzothiazole) under conventional heating and microwave irradiation. In this manner, different arylbromides such as bromobenzene, *p*-tolylbromobenzene and *p*-methoxybromobenzene were converted to their corresponding sulfides in high to excellent yields (Table 3). One interesting example is 4-(1,3-benzothiazol-2-ylthio)aniline (**3d**) which is the precursor of cathepsin-D inhibitor. So, this simplified strategy can be potentially utilized for accessing a broad range of pharmaceutically important molecules.[55]

Table 4 Synthesis of disulfides *via* two-fold C–S cross-coupling catalyzed by Pd_{np}-nSTDP[a]

Dibromoarene	Product	Yield[b] (%) (time) Thermal	MW
	 1D	85 (10 h)	81 (10 min)
	 2D	82 (6 h)	90 (45 min)
	 3D	81 (8 h)	85 (15 min)
	 4D	90 (6 h)	94 (12 min)
	 5D	90 (6 h)	93 (10 min)
	 6D	75 (6 h)	89 (10 min)
	 7D	85 (6 h)	85 (10 min)

[a] Reaction conditions: dibromoarene or 2,6-dibromopyridine (1 mmol), diaryl or 2,2′-dibenzothiazyl disulfide (1 mmol), TBAH (2 mmol), Pd_{np}-nSTDP (0.2 mol% Pd, 16 mg), H_2O/DMF (1 : 1, 2 mL), 80 °C or MW (230 W, 80 °C). [b] Isolated yield.

In order to further broaden the applicability of this method, we studied the one-pot C–S cross-coupling reactions of dibromoarenes with diaryl disulfides or 2,2′-dithiobis(benzothiazole) using this catalytic system. As can be seen, two-fold C–S cross-coupling reaction of 1,4-dibromobenzene, 9,10-dibromoanthracene or 2,6-dibromopyridine with di-*p*-tolyl disulfide, di-*m*-methoxyphenyl disulfide or 2,2′-dithiobis(benzothiazole) in the presence of Pd_{np}-nSTDP catalyst was performed efficiently under conventional heating and microwave irradiation and provided excellent yields of the desired coupling products (Table 4).

The products were characterized by different analytical tools such FT-IR, ^{1}H NMR, and ^{13}C NMR and elemental analysis. In addition, the compound **5D** was characterized by X-ray crystallographic analysis (CCDC 1029634,† Fig. 2).

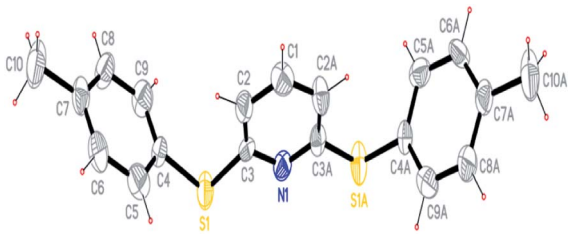


Fig. 2 Crystal structure of compound **5D**.

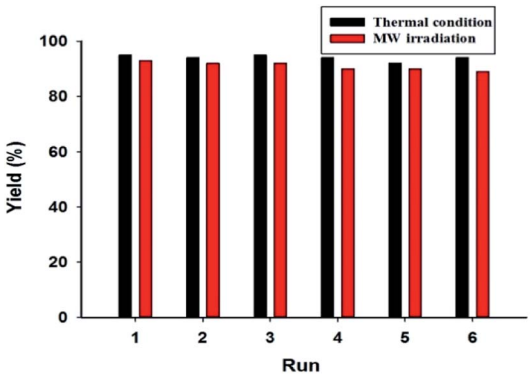
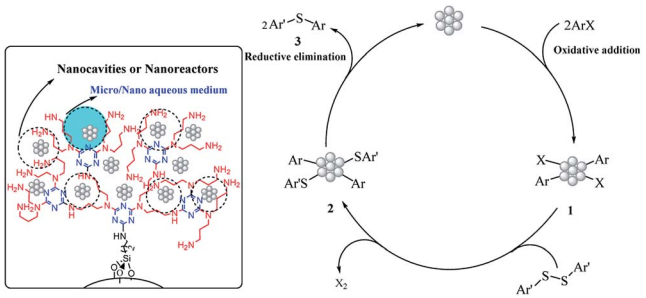


Fig. 3 Reusability of the Pd_{np}-nSTDP catalyst in the C–S cross coupling reaction of 4-bromoanisole and di-*p*-tolyl disulfide.

The recovery and reuse of a catalyst is of practical importance and is economically as well as environmentally attractive. In this manner, the recovery of Pd_{np}-nSTDP was investigated in model reaction. After completion of the reaction, ethyl acetate was added and the catalyst was separated by centrifugation. The recovered catalyst was washed with DMF, dried and reused for subsequent reactions. As shown in Fig. 3, Pd_{np}-nSTDP could be recycled and reused at least five times without any significant loss of its activity. The yields of the desired product after six consecutive runs were 93 and 89% under conventional heating and MW irradiation, which show the high efficiency of this method. Moreover, the amount of palladium leached from Pd_{np}-nSTDP catalyst, measured by ICP-OES, indicated very low leaching of palladium.

In addition, little increase in the yield of product in the hot filtration test confirmed the low leaching of the Pd species. This means that the leached Pd species are restabilized by the dendritic polymer. Therefore, it seems that the reaction mechanism is identical as a "Cocktail" of catalysts in which the Pd species are leached into the reaction medium, and then C–S coupling reaction occurs in the solution phase. After the corresponding product forms *via* reductive elimination, the leached Pd species are restabilized on the surface of the dendritic polymer.[56–58]

Based on these findings, the C–S cross-coupling mechanism is shown in Scheme 2. First, the aryl halide (ArX) is added to palladium nanoparticles *via* an oxidative-addition pathway to form the organopalladium species **1**. Then, aromatic disulfide is added to intermediate **1** to produce the intermediate **2** and released X_2.[58] Finally, the desired C–S cross-coupling product **3**



Scheme 2 Proposed mechanism for C–S cross-coupling of aryl halides and disulfides.

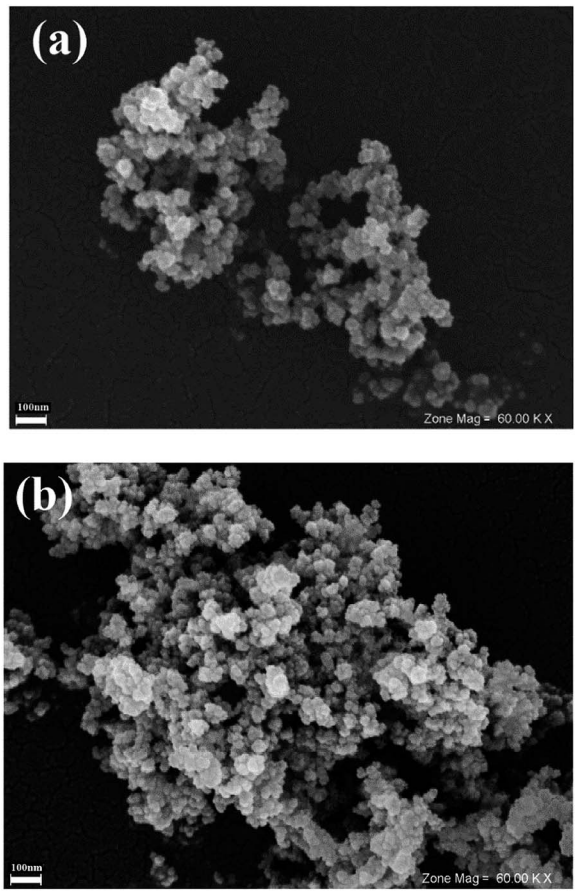


Fig. 4 FE-SEM images of (a) fresh Pd_{np}-nSTDP and (b) Pd_{np}-nSTDP after 6 runs.

is formed by a reductive-elimination process and restores the Pd_{np}-nSTDP catalyst for the next cycle.

The structure of the catalyst after the final run was also investigated by SEM and compared with the fresh Pd_{np}-nSTDP catalyst. As shown in Fig. 4, the shape and morphology of Pd_{np}-nSTDP did not show any significant change after 6^{th} run.

The applicability and reactivity of Pd_{np}-nSDTP catalyst was also compared with some other previously reported catalysts. As presented in Table 5, the Pd_{np}-nSDTP catalyst is superior in terms of TOF (h^{-1}), reaction times and amount of catalyst.

Table 5 Comparison of some results obtained in the C–S coupling reaction of diphenyl disulfide with aryl halide catalyzed by different catalysts

Catalyst and conditions	Aryl halide	Yield (%)	TOF (h^{-1})	Ref.
Cu_2S (1 mol%), Fe, K_2CO_3, DMSO, 110 °C, 18 h		95	5.28	45
$CuFe_2O_4$ (5 mol%), Cs_2CO_3, DMSO, 100 °C, 24 h		90	0.75	44
$PdCl_2$(dppf) (5 mol%), Zn, THF, reflux, 24 h		68	0.57	43
Pd_{np}-nSDTP (0.1 mol%), TBAH, DMF/H_2O, 80 °C, 3–5 h		93	310	Present work
		94	188	

Experimental

General information

The Pd_{np}-nSTDP catalyst was synthesized by our reported method.[47] Melting points were determined with a Stuart Scientific SMP2 apparatus. FT-IR spectra were recorded on a Nicolet-Impact 400D spectrophotometer. ^1H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. Elemental analysis was done on a LECO, CHNS-932 analyzer. The microwave system used in these experiments includes the following items: Micro-SYNTH labstation, equipped with a glass door, a dual magnetron system with pyramid shaped diffuser, 1000 W delivered power, exhaust system, magnetic stirrer, 'quality pressure' sensor for flammable organic solvents, and a ATCFO fiber optic system for automatic temperature control.

General procedure for synthesis of diaryl sulfides *via* C–S cross-coupling catalyzed by Pd_{np}-nSTDP

A mixture of aryl halide (1 mmol), diaryl disulfide or 2,2′-dithiobis(benzothiazole) (0.5 mmol), TBAH (1 mmol) and Pd_{np}-nSTDP (0.1 mol% Pd, 8 mg) in H_2O/DMF (1 : 1, 1 mL) was stirred at 80 °C or irradiated with MW (230 W, 80 °C) for the time indicated in Tables 2 and 3. The reaction progress was followed by TLC (eluent: ether/ethyl acetate, 5 : 1). At the end of the reaction, the mixture was cooled to room temperature, ethyl acetate (10 mL) was added and the catalyst was separated by centrifugation. The organic phase was washed with water (2 × 10 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated and the resulting crude material was purified by recrystallization from ether and ethyl acetate (5 : 1) to afford the pure product.

General procedure for synthesis of disulfides *via* two-fold C–S cross-coupling catalyzed by Pd_{np}-nSTDP

A mixture of 1,4-dibromobenzene, 9,10-dibromoanthracene or 2,6-dibromopyridine (1 mmol), diaryl/2,2′-dibenzothiazyl disulfide (1 mmol), TBAH (2 mmol) and Pd_{np}-nSTDP (0.2 mol% Pd, 16 mg) in H_2O/DMF (1 : 1, 2 mL) was stirred at 80 °C or exposed to microwave irradiation (230 W, 80 °C) for the time mentioned in Table 4. The reaction progress was check by TLC (eluent: ether/ethyl acetate, 3 : 1). When the reaction was completed, the mixture was cooled to room temperature, ethyl acetate (10 mL) was added and the catalyst was separated by centrifugation. The organic phase was washed with water (2 × 10 mL), dried over anhydrous $MgSO_4$. Evaporation of the filtrate followed by purification of the crude material by recrystallization from ethyl acetate provided the pure product.

Conclusions

In conclusion, we have developed an eco-friendly and convenient method for the preparation of a series of diaryl sulfides *via* C–S cross-coupling of aryl halides with diaryl/diheteroaryl disulfides catalyzed by Pd_{np}-nSTDP under conventional heating and microwave irradiation. This catalytic system was also efficiently used for the one-pot two-fold C–S cross-coupling reactions of dibromoarenes in high yields. The high performance as well as the recyclability of this dendritic catalyst as a nanoreactor makes this method a valid contribution compared to the existing methodologies.

Conflicts of interest

There is no conflict of interest.

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