Palladium Nanoparticles Immobilized on Nano-Silica Triazine Dendritic Polymer (Pd_{np}-nSTDP): An Efficient and Reusable Catalyst for Suzuki–Miyaura Cross-Coupling and Heck Reactions

Amir Landarani Isfahani,^a Iraj Mohammadpoor-Baltork,^{a,*} Valiollah Mirkhani,^{a,*} Ahmad R. Khosropour,^a Majid Moghadam,^a Shahram Tangestaninejad,^a and Reza Kia^b

^a Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan 81746-73441, Iran

Fax: (+98)-311-6689732; phone: (+98)-311-7932705; e-mail: imbaltork@sci.ui.ac.ir or mirkhani@sci.ui.ac.ir

^b Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran

Received: August 8, 2012; Revised: January 22, 2013; Published online: March 19, 2013

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201200707.

Abstract: A new catalyst based on palladium nanoparticles immobilized on nano-silica triazine dendritic polymer (Pd_{np} -nSTDP) was synthesized and characterized by FT-IR spectroscopy, thermogravimetric analysis, field emission scanning electron microscopy, energy dispersive X-ray, transmission electron microscopy and elemental analysis. The size of the palladium nanoparticles was determined to be $3.1 \pm$ 0.5 nm. This catalytic system showed high activity in the Suzuki–Miyaura cross-coupling of aryl iodides, bromides and chlorides with arylboronic acids and also in the Heck reaction of these aryl halides with styrenes. These reactions were best performed in a dimethylformamide (DMF)/water mixture (1:3) in the

Introduction

The application of palladium nanoparticles (PdNPs) as catalysts, especially in Suzuki-Miyaura cross-coupling and Heck reactions, has attracted great attention in the last decade.^[1] Due to their large surface-tovolume ratio, the nanoparticle-based catalytic systems exhibit higher activity than their corresponding bulk materials.^[2] However, these nanoparticles usually undergo aggregation to form larger, bulk particles and, therefore, their catalytic activities are reduced. Generally, the aggregation of nanoparticles can be avoided by using suitable stabilizers or protecting agents.^[3] The immobilization of these nanoparticle-based catalytic systems on solid supports makes the catalyst recyclable and reusable, and minimizes the leaching of the particles. These are very important aspects from environmental, economical and safety points of view.^[4]

presence of only 0.006 mol% and 0.01 mol% of the catalyst, respectively, under conventional conditions and microwave irradiation to afford the desired coupling products in high yields. The Pd_{np} -nSTDP was also used as an efficient catalyst for the preparation of a series of star- and banana-shaped compounds with a benzene, pyridine, pyrimidine or 1,3,5-triazine unit as the central core. Moreover, the catalyst could be recovered easily and reused several times without any considerable loss of its catalytic activity.

Keywords: Heck reaction; palladium nanoparticles; reusable catalyst; Suzuki–Miyaura cross-coupling; triazine dendritic polymer

Dendritic polymers are highly branched, spherical three-dimensional macromolecules, the synthesis and properties of which have attracted much attention during the past decades.^[5] Due to their three-dimensional structure and multiple internal and external functional groups, dendritic polymers can selectively act as suitable hosts for a wide range of ions and molecules.^[6] Dendritic polymers with metal ions incorporated into their core or on their surface have found great applications in catalytic processes.^[7]

Immobilization of metal-containing dendritic polymers on solid supports is of practical importance in the field of catalysis because of their easy recoverability and reusability, as well as their environmentally benign and non-polluting nature. Owing to these advantages, heterogeneous dendritic polymer-based catalysts have been efficiently used in many important organic transformations.^[8] Among dendritic molecules, triazine-based dendritic polymers have received more interest because of the low cost and chemoselective reactivity of the related starting material, cyanuric chloride (2,4,6-trichlorotriazine).^[9] Such chemoselective reactivity is temperature dependent, in which the first, second and the third substitutions proceed at 0, 25 and 70 °C, respectively. Consequently, for a wide range of catalytic applications, different generations of triazine-based dendritic polymers can be prepared *via* a stepwise functionalization and regulation of the conditions.^[10]

In continuation of our efforts on the development of efficient catalytic systems for useful synthetic organic transformations,^[11] herein we wish to report the preparation and characterization of a new thermally stable, oxygen insensitive, phosphine-free, air- and moisture-stable, and reusable palladium nanoparticles immobilized on nano-silica functionalized triazine dendritic polymer (Pd_{np} -nSTDP) catalyst and its application in C–C coupling reactions *via* the Suzuki-Miyaura cross-coupling and Heck reactions under conventional conditions and microwave irradiation (Scheme 1).

Results and Discussion

Synthesis and Characterization of Palladium Nanoparticles Immobilized on Nano-Silica Triazine Dendritic Polymer (Pd_{nn}-nSTDP)

First, nano-silica was modified with 3-aminopropyltrimethoxysilane (APTS) according to the literature procedure^[12] to afford aminopropyl-functionalized nano-silica (AP-nSiO₂). The reaction of cyanuric chloride (CC) with the surface-attached propylamine of AP-nSiO₂ was carried out at room temperature for substitution of one of the chlorine atoms yield CC1-nSiO₂. Then, CC1-nSiO₂ to was reacted with bis(3-aminopropyl)amine, H₂NCH₂CH₂CH₂NHCH₂CH₂CH₂NH₂, to give G1 which in turn was converted to CC2-nSiO₂ upon reaction with cyanuric chloride. Finally, CC2-nSiO₂ reacted with H2NCH2CH2CH2NHCH2CH2CH2NH2 which produced the nano-silica triazine dendritic polymer (G2 or nSTDP) as the support for PdNPs (Scheme 2). These processes were monitored by FT-IR, thermogravimetric analysis (TGA) and elemental analysis.

The presence of bands in the FT-IR spectra at 1580–1603 (C=N), 1480 and 2990 cm⁻¹ (C–H_{aliph}) confirms the synthesis of AP-nSiO₂, CC1-nSiO₂, G1 and G2 (Figure 1).^[13] Due to the presence of a strong Si– O band at 1000–1100 cm⁻¹, the C–Cl band of CC at 1010 cm⁻¹ was masked. Also, it was not possible to assign the N–H band in the FT-IR spectrum, due to interference from the silica O–H band (3200– 3400 cm⁻¹).

The nitrogen content of AP-nSiO₂, determined by elemental analysis, was found to be 0.99 mmol g^{-1} of nano-silica.

The amount of organic moieties in the cyanuric chloride-functionalized AP-nSiO₂ (CC1-nSiO₂) was also determined by TGA and elemental analysis. The total amount of organic moieties on nano-SiO₂ was about 0.76 mmol g^{-1} . Also, the amount of released chloride ion was determined by titration with AgNO₃, the results of which were in accordance with the results obtained by TGA and elemental analysis. The weight loss of the nSTDP between 30-600°C as a function of temperature was determined using TGA, which is an irreversible process because of thermal decomposition. The TGA plots of AP-nSiO₂, CC1-nSiO₂, CC2-nSiO₂, G1 and G2 (Figure 2) depict a two-step thermal decomposition. The first step of weight loss in the case of AP-nSiO₂ corresponds to the removal of physically adsorbed water, whereas, in the other cases, the main weight loss in the second step is due to the removal of organic moieties on the surface. The TGA results are summarized in Table 1. The observed total weight losses for AP-nSiO₂, G1 and G2 are 5.757%, 17.77% and 36.64%, respectively. On the basis of these values, the theoretical conversion is 77% for AP-nSiO₂ \rightarrow CC1-nSiO₂, 60% for CC1-nSiO₂ \rightarrow G1, 57% for G1 \rightarrow CC2-nSiO₂ and 80% for CC2-nSiO₂ \rightarrow G2. A summary of the elemental analysis and TGA data is included in Table 2. A good agreement was observed between elemental analysis and TGA data for these conversions (Table 2).

After preparation and characterization of nSTDP, the palladium nanoparticles were immobilized onto this ligand. As shown in Scheme 3, the palladium nanoparticles immobilized on nano-silica trazine den-



Scheme 1. Suzuki–Miyaura cross-coupling and Heck reaction catalyzed by Pd_{np}-nSTDP.





Scheme 2. Synthesis of nano-silica triazine dendritic polymer (G2 or nSTDP).



Figure 1. The FT-IR spectra of: a) AP-nSiO₂; b) CC1-nSiO₂; c) G1 and d) G2 (nSTDP).

Figure 2. TGA spectra of: a) AP-nSiO₂; b) CC1-nSiO₂; c) G1; d) CC2-nSiO₂ and e) G2.

Adv. Synth. Catal. 2013, 355, 957-972

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

(a)

(b)

(C)

(d)

(e)

600

959

500

Table 1. Thermogravimetric analysis (TGA) results.

Sample	Organic [wt%]	Organic [mmolg ⁻¹ n-SiO ₂]	Yield [%]
AP-nSiO ₂	5.757	0.99	_
CC1-nSiO ₂	15.58	0.76	77
G1	17.77	0.45	60
CC2-nSiO ₂	25.301	0.26	57
G2	36.64	0.21	80

Table 2. TGA and elemental analysis (EA) results for the synthesis of nano-silica triazine dendritic polymer.

		С	Н	N	Total
AP-nSiO ₂	TGA (wt%)	3.636	0.707	1.414	5.757
	EA (wt%)	3.719	1.020	1.552	6.291
CC1-nSiO ₂	TGA (wt%)	5.47	0.53	4.25	10.25
	EA (wt%)	5.537	0.832	4.040	10.409
G1	TGA (wt%)	9.722	1.751	6.310	17.783
	EA (wt%)	10.071	2.100	6.347	18.518
CC2-nSiO ₂	TGA (wt%)	12.96	1.261	11.08	25.301
	EA (wt%)	13.010	1.920	11.216	26.146
G2	TGA (wt%)	20.411	3.590	14.11	38.111
	EA (wt%)	20.411	4.209	14.187	38.807

dritic polymer (Pd_{np} -nSTDP) were prepared by reduction of $Na_2Pd_2Cl_6^{[14]}$ (prepared *in situ* from $PdCl_2$ and NaCl) in methanol at 60 °C in the presence of nSTDP. The morphology of the surfaces of nSTDP and

Pd_{np}-nSTDP were studied by field emission scanning

electron microscopy (FE-SEM) (Figure 3). The size and surface morphologies of the nSTDP and Pd_{np} nSTDP were directly visualized by FE-SEM (Figure 3a and b). As can be seen the nSiO₂ particles are spherical and have diameters in the range of 40 to 70 nm.

The energy dispersive X-ray (EDX) results, obtained from SEM analysis for the nSTDP and Pd_{np} nSTDP, are shown in Figure 3c and d, which clearly show the presence of Pd nanoparticles in the Pd_{np} nSTDP catalyst.

Further characterization of Pd_{np} -nSTDP was performed by transmission electron microscopy (TEM). The TEM images of Pd_{np} -nSTDP showed well-defined spherical Pd particles dispersed in nSTDP (Figure 4). The size distribution of Pd nanoparticles was about 3.1 ± 0.5 nm, indicating that palladium nanoparticles did not aggregate upon immobilization on nSTDP. All these observations indicate that the triazine dendritic polymer is a good host and ligand for palladium nanoparticles.

The palladium content of the catalyst, measured by ICP, showed a value of 1.27% (0.12 mmolg⁻¹ of nSTDP).

Suzuki–Miyaura Cross-Coupling of Aryl Halides with Arylboronic Acids at Room Temperature and under MW Irradiation

Initially, the Suzuki–Miyaura cross-coupling of 4-bromoacetophenone with phenylboronic acid in the presence of Pd_{np} -nSTDP catalyst was chosen as a model



Scheme 3. Synthesis of the Pd_{np}-nSTDP catalyst.

960 asc.wiley-vch.de



Figure 3. FE-SEM images of: a) nSTDP and b) Pd_{np} -nSTDP. SEM-EDX spectra of: c) nSTDP and d) Pd_{np} -nSTDP.

for optimization of reaction parameters such as the base and solvent types, temperature, catalyst loading,



Figure 4. TEM image and particle size distribution results for Pd_{np} -nSTDP catalyst.

molar ratios of substrates and MW power. The results are summarized in Table 3. The model reaction was

Table 3. Optimization of the Suzuki-Miyaura cross-coupling of 4-bromoacetophenone (BA) with phenylboronic acid (PBA) catalyzed by Pd_{np}-nSTDP.

		Br	B(OH) ₂ -	Pd _{np} -nSTDP K ₂ CO ₃ , Solvent r.t. or MW	Ph		
Entry	Base	Ba:PBA:Base [mmol]	Catalyst [mol% Pd]	Solvent ^[a]	Method	Time [h]	Yield [%] ^[b]
1	NEt ₃	1:1.1:1.5	0.006	DMF/H ₂ O (1:3)	r.t.	24	35
2	$DBU^{[c]}$	1:1.1:1.5	0.006	$DMF/H_2O(1:3)$	r.t.	24	42
3	piperidine	1:1.1:1.5	0.006	$DMF/H_2O(1:3)$	r.t.	24	25
4	NaOH	1:1.1:1.5	0.006	$DMF/H_2O(1:3)$	r.t.	24	58
5	K_3PO_4	1:1.1:1.5	0.006	$DMF/H_2O(1:3)$	r.t.	24	50
6	Na ₂ CO ₃	1:1.1:1.5	0.006	$DMF/H_2O(1:3)$	r.t.	14	73
7	K_2CO_3	1:1.1:1.5	0.006	$DMF/H_2O(1:3)$	r.t.	7	95
8	K_2CO_3	1:1.1:1.5	0.006	$DMF/H_2O(1:1)$	r.t.	16	64
9	K_2CO_3	1:1.1: 1.5	0.006	toluene	r.t.	18	58
10	K_2CO_3	1:1.1: 1.5	0.006	DMF	r.t.	15	70
11	K_2CO_3	1:1.1: 1.5	0.006	H_2O	r.t.	15	61
12	K_2CO_3	1:1.1: 1.5	0.006	EtOH	r.t.	14	53
13	K_2CO_3	1:1.1: 1.5	0.006	$H_2O/EtOH$ (1:1)	r.t.	14	60
14	K_2CO_3	1:1:1	0.006	DMF/H_2O (1:3)	r.t.	14	60
15	K_2CO_3	1:1.1:1.2	0.006	$DMF/H_2O(1:3)$	r.t.	11	72
16	K_2CO_3	1:1.1:1.5	0.004	DMF/H ₂ O (1:3)	r.t.	12	70
17	K_2CO_3	1:1.1: 1.5	0.008	$DMF/H_2O(1:3)$	r.t.	7	95
18 ^[d]	K_2CO_3	1:1.1:1.5	0.006	DMF/H ₂ O (1:3)	r.t.	7	93
19 ^[e]	K_2CO_3	1:1.1:1.5	0.006	$DMF/H_2O(1:3)$	r.t.	7	94
20	K_2CO_3	1:1:1	0.006	DMF/H ₂ O (1:3)	MW (200 W, 70 °C)	9 min	68
21	K_2CO_3	1:1.1:1.2	0.006	$DMF/H_2O(1:3)$	MW (200 W, 70 °C)	8 min	75
22	K_2CO_3	1:1.1: 1.5	0.004	$DMF/H_2O(1:3)$	MW (200 W, 70 °C)	6 min	73
23	K_2CO_3	1:1.1:1.5	0.006	$DMF/H_2O(1:3)$	MW (200 W, 70 °C)	5 min	93
24	K_2CO_3	1:1.1:1.5	0.008	$DMF/H_2O(1:3)$	MW (200 W, 70 °C)	5 min	93
25	K_2CO_3	1:1.1:1.5	0.006	$DMF/H_2O(1:3)$	MW (180 W, 50 °C)	12 min	62
26	K_2CO_3	1:1.1:1.5	0.006	$DMF/H_2O(1:3)$	MW (250 W, 85 °C)	5 min	93

[a] Reaction was performed using 2 mL of solvent.

[b] Isolated yield.

[c] DBU=1,8-diazabicyclo[5.4.0]undec-7-ene.

^[d] Reaction was performed under an argon atmosphere.

^[e] Reaction was performed under an oxygen atmosphere.

first performed in the presence of different organic and inorganic bases such as NEt₃, DBU, piperidine, NaOH, K_3PO_4 , Na₂CO₃ and K_2CO_3 ; amongst them K_2CO_3 was found to be the most effective base. Then, the same reaction was carried out in different single and mixed solvents. Among the solvents examined, DMF/H₂O (1:3) was proved to be the best reaction medium. The effects of the amount of catalyst and the ratios of substrates on the model reaction were also explored; the best result was obtained using 0.006 mol% Pd catalyst and the ratio of 4-bromoacetophenone to phenylboronic acid was 1:1.1. Therefore, it was concluded that the optimum reaction conditions involved 4-bromoacetophenone (1 mmol), phenylboronic acid (1.1 mmol), K₂CO₃ (1.5 mmol) and Pd_{np}-nSTDP (0.006 mol% Pd) in DMF/H₂O (1:3) at room temperature (Table 3, entry 7).

For reaction under MW irradiation, the above-mentioned molar ratios of the reactants and catalyst with an applied power of 200 W at 70 °C were found to be the optimal conditions (Table 3, entry 23). It is noteworthy that the model reaction was also carried out under argon and oxygen atmospheres; the results were comparable to that obtained in an open system (Table 3, entries, 18 and 19), which clearly reveals that the Pd_{np}-nSTDP is a stable and oxygen-insensitive catalyst.

Encouraged by our initial studies, we then examined the generality and versatility of this supported palladium-catalyzed Suzuki-Miyaura cross-coupling of aryl halides with arylboronic acids.

As can be seen in Table 4, under the optimized conditions, a diversity of aryl iodides and bromides containing electron-donating and electron-withdrawing substituents reacted efficiently with phenylboronic

		$X \leftarrow R^2 \frac{1}{r}$	B(OH) ₂ -	Pd _{np} -nSTDP (0 DMF/H ₂ O (1:3) K ₂ CO ₃ (1.5 mr r.t. or MW	0.006 mol% Pd)) nol)		
Entry	\mathbf{R}^1	\mathbb{R}^2	Х	Room T Time [h]	emperature Yield [%] ^[b]	M Time [min]	W Yield [%] ^[b]
1	Н	Н	Ι	2	95	2	95
2	Η	4-MeO	Ι	3	96	2	92
3	4-Ac	Η	Ι	2	96	2	93
4	4-Me	Η	Ι	2	95	3	96
5	4-Ac	4-MeO	Ι	3	96	3	95
6	Η	Η	Br	6	95	3	94
7	Η	4-MeO	Br	7	94	3	95
8	4-MeO	Η	Br	6	96	3	93
9	4-MeO	4-MeO	Br	6.5	95	3	94
10	4-Ac	Н	Br	7	95	5	93
11	4-Ac	4-MeO	Br	8	95	5	95
12	4-CHO	Н	Br	10	90	5	92
13	4-CHO	4-MeO	Br	10	92	5	91
14	3-CN	Η	Br	8	94	4	92
15	Н	Н	Cl	18 (10 ^[c])	84 (92 ^[c])	10	94
16	Η	4-MeO	Cl	$24 (14^{[c]})$	84 (90 ^[c])	10	90
17	4-Ac	Н	Cl	$20(10^{[c]})$	83 (92 ^[c])	7	92
18	4-Ac	4-MeO	Cl	$18(10^{[c]})$	81 (95 ^[c])	8	93
19	4-CHO	Н	Cl	$18 (10^{[c]})$	80 (90 ^[c])	8	90

Table 4. Suzuki-Miyaura cross-coupling of aryl halides with arylboronic acids catalyzed by Pdnp-nSTDP.^[a]

[a] Reaction conditions: aryl halide (1 mmol), arylboronic acid (1.1 mmol), K₂CO₃ (1.5 mmol), Pd_{np}-nSTDP (0.006 mol% Pd), DMF/H₂O (1:3, 2 mL), r.t. or MW (200 W, 70 °C).

^[b] Isolated yield.

^[c] Reaction was performed at 80 °C.

acid and 4-methoxyphenylboronic acid under air atmosphere at room temperature to afford the desired cross-coupling products in high yields (Table 4, entries 1–14). The experimental results showed that the electronic properties of the substituents on the aromatic rings of the starting materials had no significant influence on the reaction, however, aryl iodides were found to be more reactive than aryl bromides.

It is important to note that aryl chlorides are cheaper and more readily available but less reactive than aryl iodides and bromides. Due to lower reactivity, the coupling reactions with aryl chlorides have been generally investigated using a higher amount of catalyst.^[15] In order to further explore the efficiency and applicability of this method, the cross-coupling of aryl chlorides with arylboronic acids was also checked under the same conditions. As shown in Table 4, reaction of various aryl chlorides with phenylboronic acid and 4-methoxyphenylboronic acid proceeded smoothly in the presence of the same catalyst amount as used for arvl iodides and bromides (0.006 mol% Pd) at room temperature, resulting in the desired crosscoupling products in high yields (80-84%) within 18-24 h. When the same reactions were performed at 80 °C, the yields increased slightly (90–95%) but the reaction times decreased significantly (10–14 h) (Table 4, entries 15–19).

The Suzuki–Miyaura cross-coupling was also investigated under microwave irradiation. The treatment of a variety of aryl halides (iodides, bromides and chlorides) with arylboronic acids under the optimized microwave irradiation, afforded the corresponding cross-coupling products in 90–96% yields in very short reaction times (2–10 min) (Table 4). The results reveal that the yields of the products are comparable under conventional conditions and microwave irradiation, but the reaction times are considerably shorter under microwave irradiation (Table 4). It is notable that various sensitive functional groups such as MeO, Ac, CHO and CN are well tolerated under the reaction conditions.

Heck Reaction of Aryl Halides with Styrenes Under Thermal Conditions and MW Irradiation

Encouraged by the obtained results in the Suzuki-Miyaura cross-coupling, we then investigated the potential of our Pd_{nv}-nSTDP catalyst in the Heck reaction. In order to obtain the optimum experimental conditions, the reaction of 4-bromoacetophenone with styrene was considered as a model reaction in the presence of Pd_{np}-nSTDP catalyst under thermal conditions and microwave irradiation. The effects of the reaction conditions such as the type of base and solvent, temperature, catalyst amount, molar ratios of substrates and MW power were tested and a summary of the optimization experiments is provided in Table 5. As can be seen, under thermal conditions, the best result was obtained using 4-bromoacetophe-K₂CO₃ none (1 mmol),styrene (1.1 mmol), (1.5 mmol) and Pd_{np}-nSTDP (0.01 mol% Pd) in DMF/ H_2O (1:3) at 85°C (Table 5, entry 7). When the same

Ö

reaction was exposed to MW irradiation, the maximum yield of the desired product was achieved with a MW power of 200 W at 70 °C (Table 5, entry 22).

Using the optimized reaction conditions, a variety of structurally divergent aryl iodides, bromides and chlorides was coupled with styrene and 4-methylstyrene to generate the desired coupling products in 88– 95% yields at 85 °C within 9–22 h (Table 6). The Heck reaction of these aryl halides with styrenes was also examined under microwave irradiation. Under these conditions, the corresponding coupling products were obtained in 87–96% yields in 8–20 min (Table 6). The experimental results show that microwave irradiation has the evident advantage of short reaction times over the traditional heating mode. It is notewor-

0

Table 5. Optimization of the Heck reaction of 4-bromoacetophenone (BA) with styrene (Sty) catalyzed by Pd_{np}-nSTDP.

				Pd _{np} -nSTDP			
	Br			base, solvent thermal or MW	Ph		
Entry	Base	BA:Sty:K ₂ CO ₃ [mmol]	Catalyst [mol% Pd]	Solvent ^[a]	Method	Time [h]	Yield [%] ^[b]
1	NEt ₃	1:1.1:1.5	0.01	DMF/H ₂ O (1:3)	thermal (85°C)	30	30
2	DBU	1:1.1:1.5	0.01	$DMF/H_2O(1:3)$	thermal (85 °C)	30	39
3	piperidine	1:1.1:1.5	0.01	$DMF/H_2O(1:3)$	thermal (85 °C)	30	48
4	NaOH	1:1.1:1.5	0.01	$DMF/H_2O(1:3)$	thermal (85°C)	30	48
5	K_2CO_3	1:1.1:1.5	0.01	$DMF/H_2O(1:3)$	thermal (85 °C)	24	52
6	Na ₂ CO ₃	1:1.1:1.5	0.01	DMF/H ₂ O (1:3)	thermal (85°C)	24	50
7	K_2CO_3	1:1.1:1.5	0.01	$DMF/H_2O(1:3)$	thermal (85 °C)	15	92
8	K_2CO_3	1:1:1	0.01	DMF/H ₂ O (1:3)	thermal (85°C)	24	50
9	K_2CO_3	1:1.1:1.2	0.01	$DMF/H_2O(1:3)$	thermal (85 °C)	24	50
10	K_2CO_3	1:1.1:1.5	0.01	DMF/H ₂ O (1:1)	thermal (85°C)	24	65
11	K_2CO_3	1:1.1:1.5	0.01	toluene	thermal (85 °C)	24	50
12	K_2CO_3	1:1.1:1.5	0.01	DMF	thermal (85 °C)	24	63
13	K_2CO_3	1:1.1:1.5	0.01	H_2O	thermal (85°C)	24	50
14	K_2CO_3	1:1.1:1.5	0.01	EtOH	thermal (85 °C)	30	48
15	K_2CO_3	1:1.1:1.5	0.01	H ₂ O/EtOH (1:1)	thermal (85°C)	30	40
16	K_2CO_3	1:1.1:1.5	0.008	DMF/H ₂ O (1:3)	thermal (85°C)	15	65
17	K_2CO_3	1:1.1:1.5	0.012	$DMF/H_2O(1:3)$	thermal (85 °C)	15	92
18	K_2CO_3	1:1.1:1.5	0.01	$DMF/H_2O(1:3)$	thermal (70°C)	15	85
19	K_2CO_3	1:1.1:1.5	0.01	$DMF/H_2O(1:3)$	thermal (100°C)	15	92
20	K_2CO_3	1:1.1:1.2	0.01	$DMF/H_2O(1:3)$	MW (200 W, 70°C)	12 min	70
21	K_2CO_3	1:1.1:1.5	0.008	DMF/H ₂ O (1:3)	MW (200 W, 70 °C)	12 min	68
22	K_2CO_3	1:1.1:1.5	0.01	DMF/H ₂ O (1:3)	MW (200 W, 70 °C)	12 min	93
23	K_2CO_3	1:1.1:1.5	0.012	DMF/H ₂ O (1:3)	MW (200 W, 70 °C)	12 min	93
24	K ₂ CO ₃	1:1.1:1.5	0.01	DMF/H ₂ O (1:3)	MW (250 W, 85°C)	12 min	93
25	K_2CO_3	1:1.1:1.5	0.01	DMF/H ₂ O (1:3)	MW (150 W, 50°C)	12 min	85

^[a] Reaction was performed using 2 mL of solvent.

^[b] Isolated yield.

Table 6. Heck reaction of aryl halides with styrenes catalyzed by Pd_{np}-nSTDP.^[a]

			\sim	Pd _{np} -nSTDP (0.01	mol% Pd)	$\mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} \mathbf{A} $	
				DMF/H ₂ O (1:3) K ₂ CO ₃ (1.5 mmol) 85 °C or MW			
Entry	\mathbf{R}^1	\mathbb{R}^3	Х	Th	ermal	N	ſW
				Time [h]	Yield [%] ^[b]	Time [min]	Yield [%] ^[b]
1	Н	Н	Ι	9	95	10	95
2	Н	4-Me	Ι	9	93	10	93
3	4-Me	4-Me	Ι	9	92	8	96
4	4-Ac	Н	Ι	9	95	8	96
5	4-Ac	4-Me	Ι	9	91	8	95
6	Η	Н	Br	14	90	12	93
7	Н	4-Me	Br	14	92	12	95
8	4-MeO	4-Me	Br	15	93	12	95
9	4-F	Н	Br	17	91	10	89
10	4-F	4-Me	Br	15	90	14	92
11	4-Me	Н	Br	10	93	12	93
12	4-Ac	4-Me	Br	13	95	13	92
13	4-Ac	Н	Br	15	92	12	93
14	4-CHO	Н	Br	15	90	18	89
15	Н	Н	Cl	20	92	17	93
16	4-MeO	Н	Cl	20	89	15	89
17	4-Ac	Н	Cl	22	88	20	90
18	4-Ac	4-Me	Cl	20	89	20	87
19	4-CHO	Η	Cl	20	91	15	89

[a] *Reaction conditions:* aryl halide (1 mmol), styrene (1.1 mmol), K₂CO₃ (1.5 mmol), Pd_{np}-nSTDP (0.01 mol% Pd), DMF/ H₂O (1:3, 2 mL), 85 °C or MW (200 W, 70 °C).

^[b] Isolated yield.

thy that, based on NMR spectra, in all Heck olefination reactions, the *trans*-product was obtained with 100% selectivity.

Synthesis of Star- and Banana-Shaped Molecules Containing Benzene, Pyridine, Pyrimidine or 1,3,5-Triazine Central Cores Catalyzed by Pd_{nn}-nSTDP

Star- and banana-shaped compounds are of great significance due to their wide variety of applications as liquid crystals,^[16] components of organic light-emitting devices (OLEDs),^[17] field-effect transistors (FETs),^[18] single molecular electronics,^[19] and non-linear optical materials.^[20] They have also been used in coordination chemistry,^[21] and in the syntheses of dendritic chromophores^[22] and hyperbranched conjugated molecules.^[23] Accordingly, the development of new and highly efficient methods for their preparation is a desirable synthetic goal.

In order to further widen the applicability of this method, we examined the preparation of a range of

Table 7. Synthesis of star- and banana-shaped molecules via Suzuki-ivityadia cross-coupling catalyzed by $I u_{nn}$ -iis i

Entry	Substrate	Product		Room T Time [h]	èmperature Yield [%] ^[a]	M Time [min]	W Yield [%] ^[a]
1	Br		S1 ^[b]	12	92	8	95
2	Br	o C N C o	S2 ^[b]	12	92	8	93

Adv. Synth. Catal. 2013, 355, 957-972

asc.wiley-vch.de

Table 7. (Continued)

Entrv	Substrate		Room Temperature		MW		
				Time [h]	Yield [%] ^[a]	Time [min]	Yield [%] ^[a]
3	Br Br		S3 ^[c]	14	90	8	94
4	Br Br		S4 ^[c]	14	89	8	92
5			85 ^[d]	15	90	10	93
6			S6 ^[d]	15	91	10	89
7			S7 ^[d]	15	83	10	87
8			S8 ^[d]	15	87	10	90

^[a] Isolated yield.

^[b] *Reaction conditions:* 2,6-dibromopyridine (1 mmol), arylboronic acid (2.3 mmol), K₂CO₃ (3 mmol), Pd_{np}-nSTDP (0.012 mol% Pd), DMF/H₂O (1:3, 8 mL), room temperature or MW (200 W, 70 °C).

^[c] *Reaction conditions:* 1,3,5-tribromobenzene (1 mmol), arylboronic acid (3.8 mmol), K₂CO₃ (4.5 mmol), Pd_{np}-nSTDP (0.018 mol% Pd), DMF/H₂O (1:3, 8 mL), room temperature or MW (200 W, 70 °C).

^[d] Reaction conditions: 2,4,6-tricholoropyrimidine or 2,4,6-trichlorotriazine (1 mmol), arylboronic acid (4.2 mmol), K₂CO₃ (4.5 mmol), Pd_{np}-nSTDP (0.045 mol% Pd), DMF/H₂O (1:1, 8 mL), room temperature or MW (200 W, 70 °C).

star- and banana-shaped molecules using this catalytic system. The results are summarized in Table 7. As the data demonstrated, the Suzuki-Miyaura cross-coupling of 2,6-dibromopyridine with phenylboronic acid or 4-methoxyphenylboronic acid was performed efficiently in the presence of Pd_{np}-nSTDP catalyst at room temperature and under microwave irradiation and the corresponding banana-shaped molecules were obtained in high yields (Table 7, entries 1 and 2). Also, a series of star-shaped triarylbenzens, triarylpyrimidines and triaryltriazines was obtained in high yields using this method by coupling of 1,3,5-tribromobenzene, 2,4,6-trichloropyrimidine or 2.4.6trichlorotriazine with arylboronic acids at room temperature and under microwave irradiation (Table 7, entries 3-8).

It is noteworthy that the preparation of some starshaped molecules was studied directly from 4-bromoand 4-iodoacetophenones as precursors by a combination of cyclotrimerization and the Suzuki–Miyaura cross-coupling *via* two synthetic pathways: path a) cyclotrimerization of 4-haloacetophenones catalyzed by $H_3PW_{12}O_{40}$ (HPW)^[11a] and then cross-coupling with arylboronic acids in the presence of Pd_{np}-nSTDP catalyst; path b) cross-coupling of 4-haloacetophenones with arylboronic acids catalyzed by Pd_{np}-nSTDP and subsequent cyclotrimerization in the presence of HPW (Scheme 4). As can be seen, the path b is more effective and the desired star-shaped molecules were obtained in high yields under these conditions.

The path a) is unfavourable due to the formation of two by-products, in addition to the desired product.

For example, in the preparation of **S11** from **S9** by the Suzuki–Miyaura cross-coupling reaction with phenylboronic acid catalyzed by Pd_{np} -nSTDP, the monoand bis-cross-coupling products (**S13** and **S14**) were also produced (Scheme 5).

Finally, the efficiency of this catalytic system was examined for the synthesis of star-shaped molecules by the Heck reaction. As shown in Scheme 6, the Heck reaction of 1,3,5-tribromobenzene either with styrene or with 4-methylstyrene proceeded smoothly in the presence of Pd_{np} -nSTDP at 85 °C and under microwave irradiation, affording the corresponding star-shaped products (**S15** and **S16**) in high yields.

In Table S1 (Supporting Information) some of the results of our experiments are compared with some of those reported using several Pd-based nanoparticle catalysts.^[24,25] As can be seen, some of the reported methods provide higher yields (entries 13, 14 and 16) and/or shorter reaction times (entries 8, 13 and 17). However, in the present method, the amount of the catalyst (Pd_{np}-nSTDP) is much lower and the turnover frequencies (TOFs) are higher, and the reaction temperatures are comparable (entries 3, 7 and 16) or lower than the others.

To the best of our knowledge, this is the first report on the synthesis of palladium nanoparticles immobilized on a nano-silica triazine dendritic polymer and its application in C–C coupling reactions.

The structures of the products were determined from their spectral data. The structure of the product **S2** was additionally confirmed by X-ray diffraction analysis (Figure 5, CCDC 854353, these data can be



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

Adv. Synth. Catal. 2013, 355, 957-972



Scheme 5. Reaction of 1,3,5-tris(4-bromophenyl)benzene S9 with phenylboronic acid catalyzed by Pd_{nn}-nSTDP.



Scheme 6. Synthesis of star-shaped molecules by the Heck reaction.



Figure 5. Crystal structure of compound S2.

asc.wiley-vch.de

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

request/cif).

Catalyst Recycling and Reuse

obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_

The recycling and reusability of a catalyst is very important from practical, economical and environmental points of view. Thus, the reusability of Pd_{np}-nSTDP

was examined in the Suzuki-Miyaura cross-coupling of 4-bromoacetophenone with phenylboronic acid

under the optimized conditions. After completion of the reaction (in the case of MW irradiation, the reac-

Table 8. Recycling and reuse of the Pd_{np} -nSTDP catalyst in Suzuki–Miyaura cross-coupling of 4-bromoacetophenone with phenylboronic acid.^[a]

Run	Yield [%]	[b]	Pd leached [%] ^[c]		
	Room Temp.	MW	Room Temp.	MW	
1	95	93	2	1	
2	92	91	1	1	
3	92	91	0	0	
4	92	91	0	0	
5	92	90	0	0	
6	92	90	0	0	
7	92	90	0	0	

[a] Reaction conditions: 4-bromoacetophenone (1 mmol), phenylboronic acid (1.1 mmol), K₂CO₃ (1.5 mmol), Pd_{np}nSTDP (0.006 mol% Pd) in DMF/H₂O (1:3, 2 mL), room temperature for 7 h or MW (200 W, 70 °C) for 5 min.

^[b] Isolated yield.

^[c] Determined by ICP.

tion mixture was first cooled to room temperature), ethyl acetate (15 mL) was added, the catalyst was separated by centrifugation and reused. The results showed that the catalyst could be reused six consecutive times without significant loss of its catalytic activity (Table 8). The analysis of palladium leaching from Pd_{np}-nSTDP catalyst by ICP indicated that only a trace amount of palladium has been leached in the first two runs (Table 8).

Conclusions

In conclusion, we have demonstrated palladium nanoparticles immobilized on nano-silica triazine dendritic polymer (Pd_{np} -nSTDP) to be a highly active, air- and moisture-stable, oxygen-insensitive and highly reusable catalyst for the Suzuki-Miyaura cross-coupling and the Heck reaction of aryl iodides, bromides and chlorides with arylboronic acids and styrenes, respectively, under conventional conditions and microwave irradiation. This catalytic system was also used efficiently for the synthesis of a series of star- and banana-shaped molecules. Ease of recovery and reuse of the catalyst make this method an economic and environmentally-benign process. In addition, high yields, short reaction times, wide scope and simple work-up procedure make this method a valid contribution to the existing methodologies for C-C coupling reactions.

Experimental Section

General Remarks

The chemicals used in this work were purchased from Fluka and Merck chemical companies. Melting points were determined with a Stuart Scientific SMP2 apparatus. FT-IR spectra were recorded on a Nicolet-Impact 400D spectrophotometer. ¹H and ¹³C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer using CDCl₃ as solvent. Elemental analysis was performed on a LECO, CHNS-932 analyzer. Thermogravimetric analysis (TGA) was carried out on a Mettler TG50 instrument under air flow at a uniform heating rate of 5°Cmin⁻¹ in the range 30-600°C. The TGA instrument was re-calibrated at frequent intervals with standards; the accuracy was always better than $\pm 2.0\%$. The scanning electron microscope measurement was carried out on a Hitachi S-4700 field emission-scanning electron microscope (FE-SEM). The transmission electron microscopy (TEM) was carried out on a Philips CM10 Transmission Electron Microscope operating at 100 kV. The Pd content of the catalyst was determined by a Jarrell-Ash 1100 ICP analysis. 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.

Synthesis of Triazine Dendritic Polymer Supported on Nano-Silica (nSTDP)

Activation of Nano-Silica: In a round-bottomed flask equipped with a condenser and a magnetic stirrer, a mixture of nano-silica (10 g, 40–100 nm) and concentrated HCl (80 mL, 6 M) was heated in an oil-bath at 120 °C for 24 h. The mixture was filtered and the white powder was washed with distilled water until neutral pH. The solid was dried under vacuum at 120 °C.^[26]

Preparation of Propylamine-Functionalized Nano-Silica (**AP-nSiO**₂): In a round-bottomed flask equipped with a condenser and a magnetic stirrer, a mixture of activated nanosilica (3 g) and 3-aminopropyltrimethoxysilane (APTS) (8 mL) in 50 mL of anhydrous toluene was stirred under reflux conditions for 8 h. The reaction mixture was filtered and the solid material was washed with toluene in a continuous extraction apparatus (Soxhlet) to remove the unreacted starting material, and dried in a vacuum oven at 110 °C.^[12]

Preparation of CC1-nSiO₂: The AP-nSiO₂ (2 g, $0.99 \text{ mmol g})^{-1}$ was added to a solution of cyanuric chloride (1.85 g, 10 mmol) and diisopropylethylamine (DIPEA) (10 mmol, 1.7 mL) in THF (10 mL). The reaction mixture was shaken overnight at room temperature. The solid material was separated by filtration, washed with hot THF for 12 h in a Soxhlet apparatus to remove the unreacted starting materials and then dried in a vacuum oven at 50 °C.

Preparation of Nano-Silica-Supported Triazine Dendritic Polymer (G1): To a slurry of CC1-nSiO₂ (1 g) in DMF (12 mL) was added bis(3-aminopropyl)amine (8.11 mmol, 1 mL) and DIPEA (8.11 mmol, 1.4 mL). The reaction mixture was stirred at 80 °C for 16 h. The solid material was filtered, washed with hot ethanol for 12 h in a Soxhlet apparatus to remove the unreacted starting materials and then dried in a vacuum oven at 50 °C.

Preparation of CC2-nSiO₂: Nano-silica-supported triazine dendritic polymer, G1 (1 g, 0.45 mmol) was added to a solution of cyanuric chloride (1.66 g, 9 mmol) and DIPEA

(9 mmol, 1.56 mL) in THF (20 mL). The reaction mixture was agitated at room temperature for 16 h. The reaction mixture was filtered and the solid was washed with hot THF for 16 h in a Soxhlet apparatus to remove the unreacted starting materials. Finally, the CC2-nSiO₂ was dried in a vacuum oven at 50 °C.

Preparation of Nano-Silica-Supported Triazine Dendritic Polymer (G2 or nSTDP): To a slurry of CC2-nSiO₂ (1 g, 0.36 mmol) in DMF (20 mL) was added bis(3-aminopropyl)amine (9.36 mmol, 1.14 mL) and DIPEA (9.36 mmol, 1.61 mL). The reaction mixture was agitated at 80 °C for 16 h and then filtered. The resulting nano-silica-supported dendritic polymer (G2 or nSTDP) was washed with hot ethanol for 24 h in a Soxhlet apparatus to remove unreacted starting materials and dried in a vacuum oven at 50 °C.

Preparation of Nano-Silica Triazine Dendritic Polymer Supported Palladium Nanoparticles (Pd_{np}**-nSTDP)**

A mixture of PdCl₂ (240 mg, 1.36 mmol) and NaCl (88 mg, 1.52 mmol) in methanol (8 mL) was stirred at room temperature for 24 h and then filtered. The filtrates were diluted with methanol (40 mL) and nSTDP (1 g, 0.21 mmol) was added to this solution. The resulting mixture was stirred at 60 °C for 24 h. At the end of the reaction, the mixture was cooled to room temperature, sodium acetate (0.76 g, 9.28 mmol) was added and stirred at room temperature for 1 h. The solid was filtered, washed with methanol, water and acetone, to remove the unreacted starting materials and then dried in vacuum to afford Pd_{np}-nSTDP catalyst (1.07 g) as a light gray solid. Palladium analysis (ICP): 1.27%. Average particle diameter: 3.1 ± 0.5 nm (based on TEM and particle size analyses).

General Procedure for Suzuki–Miyaura Cross-Coupling Catalyzed by Pd_{np}-nSTDP at Room Temperature and under Microwave Irradiation

A mixture of aryl halide (1 mmol), arylboronic acid (1.1 mmol), K_2CO_3 (1.5 mmol) and Pd_{nv}-nSTDP (0.006 mol% Pd) in 2 mL of DMF/H₂O (1:3) was stirred at room temperature or exposed to microwave irradiation (200 W, 70°C) under an air atmosphere for the period of time indicated in Table 4. The progress of the reaction was monitored by TLC (eluent: ether/ethyl acetate, 6:1). After completion of the reaction, ethyl acetate (15 mL) was added (in the case of the reaction under MW irradiation, the mixture was first cooled to room temperature) and the catalyst was separated by centrifugation. The organic phase was washed with water $(2 \times 10 \text{ mL})$, dried over anhydrous MgSO₄ and evaporated. The residue was recrystallized from ethyl acetate and ether (1:3) to afford the pure product (Table 4).

General Procedure for Heck Reaction Catalyzed by Pd_{np}-nSTDP under Thermal Conditions and Microwave Irradiation

In a round-bottomed flask equipped with a condenser and a magnetic stirrer, a mixture of aryl halide (1 mmol), styrene (1.1 mmol), K_2CO_3 (1.5 mmol) and Pd_{np} -nSTDP (0.01 mol%)

Pd) in 2 mL of DMF/H₂O (1:3) was stirred at 85 °C or irradiated with MW (200 W, 70 °C) under an air atmosphere for the desired time according to Table 6. The progress of the reaction was monitored by TLC (eluent: ether/ethyl acetate, 6:1). At the end of the reaction, the mixture was cooled to room temperature, 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 over anhydrous MgSO₄. Evaporation of the solvent and purification of the crude product by recrystallization from ethyl acetate and ether (1:3) afforded the pure product (Table 6).

General Procedure for Synthesis of Star- and Banana-Shaped Molecules Containing Benzene, Pyridine, Pyrimidine or 1,3,5-Triazine Central Cores *via* Suzuki–Miyaura Cross-Coupling Catalyzed by Pd_{np}nSTDP

A mixture of 1,3,5-tribromobenzene, 2,6-dibromopyridine, 2,4,6-trichloropyrimidine or 2,4,6-trichlorotriazine (1 mmol), arylboronic acid (2.3–4.2 mmol), K_2CO_3 (3–4.5 mmol) and Pd_{np} -nSTDP (0.012–010.045 mol% Pd) in 8 mL of DMF/ H_2O (1:3) was stirred at room temperature or exposed to MW irradiation (200 W, 70 °C) for the appropriate time according to Table 7. The work-up was performed as described for Suzuki Miyaura cross-coupling and the pure product was obtained by recrystallization of the crude product from ethyl acetate and ether (1:1).

Synthesis of S11 and S12 from S9 and S10 Catalyzed by Pd_{np} -nSTDP at Room Temperature and under MW Irradiation (Scheme 4, Path a)

To a mixture of 1,3,5-tris(4-halophenyl)benzene (S9 or S10, prepared according to the previously reported method^[11a]) (1 mmol), arylboronic acid (4.5 mol) and K₂CO₃ (4.5 mmol) in 10 mL of DMF/H₂O (1:1), was added Pd_{nv}-nSTDP (0.018 mol% Pd). The reaction mixture was stirred at room temperature or exposed to MW irradiation (270 W, 70°C) for the time indicated in Scheme 4. The progress of the reaction was monitored by TLC (eluent: ether/EtOAc, 9:1). After completion of the reaction, ethyl acetate (15 mL) was added (in the case of the reaction under MW irradiation, the mixture was first cooled to room temperature) and the catalyst was separated by centrifugation. The organic phase was washed with water (2×10 mL), dried over anhydrous MgSO₄, and evaporated. The resulting crude material was purified by recrystallization from ethyl acetate and ether (1:1) to afford the pure product.

Synthesis of S11 and S12 by Suzuki–Miyaura Cross-Coupling and Subsequent Cyclotrimerization (Scheme 4, Path b)

In this protocol, the reaction was performed in two steps. First, the desired 4-arylacetophenone was prepared by the reaction of 4-haloacetophenone with arylboronic acid according to the above-mentioned general procedure for Suzuki–Miyaura cross-coupling catalyzed by Pd_{np} -nSTDP (Table 4, entries 3, 5, 10 and 11). Then, the cyclotrimerization of 4-arylacetophenone was carried out according to the reported procedure.^[11a] In this step, a mixture of 4-arylaceto-

phenone (1 mmol) and $H_3PW_{12}O_{40}$ (151 mol%) was subjected to MW irradiation (450 W, 90 °C) for the appropriate time according to Scheme 4. After completion of the reaction, as monitored by TLC, hot ethyl acetate (10 mL) was added and the catalyst was separated by filtration. The solvent was evaporated and the resulting crude material was purified by recrystallization from ethyl acetate and ether (1:1) to afford the pure product.

Synthesis of 1,3,5-Tristyrylbenzenes (S15 and S16) *via* Heck Reaction Catalyzed by Pd_{np}-nSTDP under Thermal Conditions and Microwave Irradiation

The 1,3,5-tribromobenzene (1 mmol), styrene (5.5 mmol), K_2CO_3 (4.5 mmol) and Pd_{np} -nSTDP (0.08 mol% Pd) were mixed in DMF/H₂O (1:1, 10 mL). The reaction mixture was stirred at 85 °C or irradiated with MW (300 W, 85 °C) for the appropriate time as mentioned in Scheme 6. The reaction progress was monitored by TLC (eluent: ethyl acetate/ether, 1:6). After completion of the reaction, the mixture was cooled to room temperature, ethyl acetate (15 mL) was added and the catalyst was separated by centrifugation. The organic phase was washed with water (2×10 mL), dried over anhydrous MgSO₄, and evaporated. The organic phase was recrystallized from *n*-hexane to afford the pure product.

Acknowledgements

The authors are grateful to the Center of Excellence of Chemistry and Research Council of the University of Isfahan for financial support of this work.

References

- [1] A. Balanta, C. Godard, C. Claver, *Chem. Soc. Rev.* **2011**, *40*, 4973–4985.
- [2] C. Burda, X. Chen, R. Narayanan, M. A. El-Sayed, *Chem. Rev.* 2005, 105, 1025–1102.
- [3] D. Astruc, *Tetrahedron: Asymmetry* 2010, 21, 1041–1054; L. S. Ott, R. G. Finke, *Coord. Chem. Rev.* 2007, 251, 1075–1100.
- [4] a) L. Yin, J. Liebscher, *Chem. Rev.* 2007, 107, 133–173;
 b) S. Shylesh, V. Schünemann, W. R. Thiel, *Angew. Chem.* 2010, 122, 3504–3537; *Angew. Chem. Int. Ed.* 2010, 49, 3428–3459; c) M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet, F.-X. Felpin, *Adv. Synth. Catal.* 2010, 352, 33–79.
- [5] a) F. Vögtle, G. Richardt, N. Werner, *Dendrimer Chemistry*, Wiley-VCH, Weinheim, **2009**; b) D. Astruc, E. Boisselier, C. Ornelas, *Chem. Rev.* **2010**, *110*, 1857–1959.
- [6] a) G. R. Newkome, C. N. Moorefield, *Chem. Rev.* 1999, 99, 1689–1746; b) A. W. Bosman, E. W. Jensen, E. W. Meijer, *Chem. Rev.* 1999, 99, 1665–1688; c) M. W. P. L. Baars, R. Klepingler, M. H. J. Koch, S. L. Yeu, E. W. Meijer, *Angew. Chem.* 2000, 112, 1341–1344; *Angew. Chem. Int. Ed.* 2000, 39, 1341–1344.

- [7] a) K. Vassilev, S. Turmanova, M. Dimitrova, S. Boneva, *Eur. Polym. J.* 2009, 45, 2269–2278; b) A. Berger, R. J. M. K. Gebbink, G. van Koten, *Top. Organomet. Chem.* 2006, 20, 1–38; c) C. Ornelas, J. R. Aranzaes, L. Salmon, D. Astruc, *Chem. Eur. J.* 2008, 14, 50–64; d) C. Hajji, R. Haag, *Top. Organomet. Chem.* 2006, 20, 149– 176; e) L. Wu, Z.-W. Li, F. Zhang, Y.-M. He, Q.-H. Fan, *Adv. Synth. Catal.* 2008, 350, 846–862; f) C. Ornelas, J. Ruiz, L. Salmon, D. Astruc, *Adv. Synth. Catal.* 2008, 350, 837–845.
- [8] a) S. Antebi, P. Arya, L. E. Manzer, H. Alper, J. Org. Chem. 2002, 67, 6623–6631; b) P. P. Zweni, H. Alper, Adv. Synth. Catal. 2004, 346, 849–854; c) R. Touzani, H. Alper, J. Mol. Catal. A: Chem. 2005, 227, 197–207; d) J. P. K. Reynhardt, Y. Yang, A. Sayari, H. Alper, Adv. Synth. Catal. 2005, 347, 1379–1388; e) P. P. Zweni, H. Alper, Adv. Synth. Catal. 2006, 348, 725–731; f) W. Huang, J. N. Kuhn, C.-K. Tsung, Y. Zhang, S. E. Habas, P. Yang, G. A. Somorjai, Nano Lett. 2008, 8, 2027–2034; g) G. Jayamurugan, C. P. Umesh, N. Jayaraman, J. Mol. Catal. A: Chem. 2009, 307, 142–148; h) H. Hagiwara, H. Sasaki, N. Tsubokawa, T. Hoshi, T. Suzuki, T. Tsuda, S. Kuwabata, Synlett 2010, 1990–1996.
- [9] a) M. B. Steffensen, E. E. Simanek, Org. Lett. 2003, 5, 2359–2361; b) S. Yoo, J. D. Lunn, S. Gonzalez, J. A. Ristich, E. E. Simanek, D. F. Shantz, Chem. Mater. 2006, 18, 2935–2942; c) S. J. Dilly, S. J. Carlisle, A. J. Clark, A. R. Sheperd, S C. Smith, P. C. Taylor, A. Marsh, J. Polym. Sci. Part A: Polym. Chem. 2006, 44, 2248–2259; d) E. E. Simanek, H. Abdou, S. Lalwani, J. Lim, M. Mintzer, V. J. Venditto, B. Vittur, Proc. R. Soc. London Ser. A 2010, 466, 1445–1468.
- [10] M. P. Kapoor, H. Kuroda, M. Yanagi, H. Nanbu, L. R. Juneja, *Top. Catal.* **2009**, *52*, 634–642.
- [11] a) R. Ghanbaripour, I. Mohammadpoor-Baltork, M. Moghadam, A. R. Khosropour, S. Tangestaninejad, V. Mirkhani, *Polyhedron* 2012, *31*, 721–728; b) S. Safaei, I. Mohammadpoor-Baltork, A. R. Khosropour, M. Moghadam, S. Tangestaninejad, V. Mirkhani, *Adv. Synth. Catal.* 2012, *354*, 3095–3104.
- [12] N. Tsubokawa, H. Ichioka, T. Satoh, S. Hayashi, K. Fujiki, *React. Funct. Polym.* **1998**, *31*, 75–82.
- [13] R. M. Silverstein, G. C. Bassler, T. C. Morril, Spectrometric Identification of Organic Compounds, 6th edn., Wiley, New York, 1998.
- [14] R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, F. Petrucci, A. Prastaro, S. Niembro, A. Shafird, A. Vallribera, *Green Chem.* 2010, 12, 150–158.
- [15] a) C. L. Deng, S. M. Guo, Y. X. Xie, J. H. Li, *Eur. J. Org. Chem.* 2007, 1457–1462; b) I. D. Kostas, B. R. Steele, A. Terzis, S. V. Amosova, A. V. Martynov, N. A. Makhaeva, *Eur. J. Inorg. Chem.* 2006, 2642–2646; c) Q. Luo, S. Eibauer, O. Reiser, *J. Mol. Catal. A: Chem.* 2007, 268, 65–69; d) I. D. Kostas, F. J. Andreadaki, D. Kovala-Demertzi, C. Prentjas, M. A. Demertzis, *Tetrahedron Lett.* 2005, 46, 1967–1970; e) T. Mino, Y. Shirae, M. Sakamoto, T. Fujita, *J. Org. Chem.* 2005, 70, 2191–2194; f) A. Corma, H. Garcia, A. Leyva, *J. Catal.* 2006, 240, 87–99.
- [16] a) G. W. Gray, M. Hird, K. J. Toyne, *Mol. Cryst. Liq. Cryst.* 1991, 195, 221–237; b) F. Lincker, P. Bourgun, P.

Adv. Synth. Catal. 2013, 355, 957-972

Masson, P. Dider, L. Guidoni, J.-Y. Bigot, J.-F. Nicoud, B. Donnio, D. Guillon, *Org. Lett.* **2005**, *7*, 1505–1508.

- [17] a) A. Kraft, A. C. Grimsdale, A. B. Holmes, Angew. Chem. 1998, 110, 416–443; Angew. Chem. Int. Ed. 1998, 37, 402–428; b) U. Mitschke, P. Bäuerle, J. Mater. Chem. 2000, 10, 1471–1509; c) S.-C. Lo, P. L. Burn, Chem. Rev. 2007, 107, 1097–1116.
- [18] a) D. H. Kim, Y. D. Park, Y. Jang, H. Yang, Y. H. Kim, J. I. Han, D. G. Moon, S. Park, T. Chang, C. Chang, M. Joo, C. Y. Ryu, K. Cho, *Adv. Funct. Mater.* **2005**, *15*, 77–82; b) M. Funahashi, F. Zhang, N. Tamaoki, *Adv. Mater.* **2007**, *19*, 353–358.
- [19] a) J. M. Tour, *Chem. Rev.* **1996**, *96*, 537–554; b) C. Wang, A. S. Batsanov, M. R. Bryce, I. Sage, *Org. Lett.* **2004**, *6*, 2181–2184; c) A. Blaszczyk, M. Chadim, C. von Hänisch, M. Mayor, *Eur. J. Org. Chem.* **2006**, 3809–3825.
- [20] a) A. Hayek, F. Bolze, J.-F. Nicoud, P. L. Baldeck, Y. Mély, *Photochem. Photobiol. Sci.* 2000, *5*, 102–106;
 b) F. Cherioux, A.-J. Attias, H. Maillotte, *Adv. Funct. Mater.* 2002, *12*, 203–208; c) J. Wang, M. Lu, Y. Pan, Z. Peng, *J. Org. Chem.* 2002, *67*, 7781–7786.
- [21] a) J. Pang, E. J.-P. Marcotte, C. Seward, R. S. Brown, S. Wang, Angew. Chem. 2001, 113, 4166–4169; Angew. Chem. Int. Ed. 2001, 40, 4042–4045; b) A. de La Hoz, A. Dí'az-Ortiz, J. Elguero, L. J. Martí'nez, A. Moreno, A. Sánchez-Migallón, Tetrahedron 2001, 57, 4397–4403; c) P. K. Thallapally, R. K. R. Jetti, A. K. Katz, H. L. Carrell, K. Singh, K. Lahiri, S. Kotha, R. Boese, G. R. Desiraju, Angew. Chem. 2004, 116, 1169–1175; Angew. Chem. Int. Ed. 2004, 43, 1149–1155.

- [22] a) J. Palomero, J. A. Mata, F. González, E. Peris, New. J. Chem. 2002, 26, 291–297; b) S. Achelle, Y. Ramondenc, F. Marsais, N. Plé, Eur. J. Org. Chem. 2008, 3129–3140; c) S. Kotha, D. Kashinath, K. Lahiri, R. B. Sunoj, Eur. J. Org. Chem. 2004, 4003–4013.
- [23] Q. He, H. Huang, J. Yang, H. Lin, F. Bai, J. Mater. Chem. 2003, 13, 1085–1089.
- [24] a) H. Hattori, K.-I. Fujita, T. Muraki, A. Sakaba, Tetrahedron Lett. 2007, 48, 6817–6820; b) W. Chen, P. Li, L. Wang, Tetrahedron 2011, 67, 318–325; c) A. Houdayer, R. Schneider, D. Billaud, J. Ghanbaja, J. Lambert, Appl. Organomet. Chem. 2005, 19, 1239–1248; d) N. Iranpoor, H. Firouzabadi, S. Motevalli, M. Talebi, J. Organomet. Chem. 2012, 708–709, 118–124; e) K. K. Senapati, S. Roy, C. Borgohain, P. Phukan, J. Mol. Catal. A: Chem. 2012, 352, 128–134; f) M. Lakshmi Kantam, K. B. Shiva Kumar, P. Srinivas, B. Sreedhara, Adv. Synth. Catal. 2007, 349, 1141–1149; g) C. B. Putta, S. Ghosh, Adv. Synth. Catal. 2011, 353, 1889-1896.
- [25] a) V. Polshettiwar, P. Hesemann, J. J. E. Moreau, *Tetrahedron Lett.* 2007, 48, 5363–5366; b) T. Rama Krishna, N. Jayaraman, *Tetrahedron* 2004, 60, 10325–10334; c) Y. He, C. Cai, *Appl. Organomet. Chem.* 2011, 25, 799–803; d) C. M. Crudden, M. Sateesh, R. Lewis, *J. Am. Chem. Soc.* 2005, *127*, 10045–10050; e) J. D. Senra, L. F. B. Malta, A. L. F. Souza, L. C. S. Aguiar, O. A. C. Antunes, *Adv. Synth. Catal.* 2008, *350*, 2551–2558; f) S. Schweizer, J.-M. Becht, C. L. Drian, *Adv. Synth. Catal.* 2007, *349*, 1150–1158; g) P. Li, L. Wang, L. Zhang, G.-W. Wang, *Adv. Synth. Catal.* 2012, *354*, 1307–1318.
- [26] B. Karimi, A. A. Safari, J. Organomet. Chem. 2008, 693, 2967–2970.

972