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Palladium supported SBA-functionalizd 1,2-dicarboxylic acid: The first Pd-based heterogeneous synthesis of fluorenones

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ABSTRACT

The first Pd-based heterogeneous homo- and cross-coupling reactions for the fluorenones synthesis are reported. The palladium supported SBA-functionalizd 1,2-dicarboxylic acid (Pd@DCA-SBA) was prepared and characterized by the FT-IR, TGA, AAS, TEM, and EDS measurements. The prepared catalyst exhibited a high performance in some homo and cross coupling reactions for the synthesis of fluorenone derivatives using 2-bromo or 2,7-dibromo fluorenone in ethanol-water as green solvent medium.

1. Introduction

These days, the green chemistry is one of the most important research activities for chemists in both laboratory and industry. Therefore, many efficient, eco-friendly and clean synthetic methods have been developed for the synthesis of biologically and industrially active molecules [1]. The heterogeneous catalyzed coupling reactions in order to C—C bond formation are a one of the substantial areas of green chemistry research [2]. The metal-catalyzed coupling reactions play an important role for the preparation of complex molecules such as dyes, pharmaceuticals, natural products, functional materials, agrochemicals and herbicides [3]. Palladium is a widely applied metal for the wide range of coupling reactions and a number of homogeneous catalytic systems like phosphines [4], palladacycle complexes [5], Schiff base ligands [6], and *N*-heterocyclic carbenes [7] have been reported for this transformation. Eventually, these homogeneous systems have several inherent limitations such as high catalyst loading, catalyst separation and recycling, and contamination of product with traces of heavy metals. Consequently, various supported Pd catalysts with improved recycling and recovery properties have been reported to overcome this drawbacks [2,8]. Because of the good accessibility and porosity, mechanical stability, relatively low cost, high thermal, and good catalytic performance, SBA-15 and MCM-41 as mesoporous silica materials remain the most popular choice as support [9]. In fact, the reduction of the time and energy for achieving chemical transformations and separations is the main aim of these attempts. Recently, interest in palladium supported on SBA-based heterogeneous catalysts in green media is dramatically increasing from a sustainable chemistry point of view [10].

Fluorenone as a polycyclic aromatic compounds find an ever growing application in medicinal chemistry and photoelectric material science (Fig. 1) [11]. The fluorenone moiety is found in natural biologically active compounds [12]. For example, dendroflorin (**I**) is a natural product isolated from the *Dendrobium densiflorum* and have a good performance in antioxidant activity [12][12b]. Tilorone (**II**), trade names Amixin, Lavomax, as interferon-inducer is used as an antiviral drug and was found to possess potent affinity for the agonist site of the α7 neuronal nicotinic receptor [13]. The gold diethynylfluorene (**III**) was shown to possess a significant cytotoxic activity on human cancer cells [14]. Polyfluorenes and oligofluorenes are very important candidates for blue light-emitting materials [15]. Two aryl substituted fluorenone compounds DPF (**IV**) and MDPF (**V**) as organic luminescence materials was synthesized and exhibited prominent aggregation-induced enhanced emission with high solid-state fluorescence quantum yields [16]. Bisfluorenone (**VI**) has been synthesized as potential solute in liquid scintillation detector systems [17]. Therefore, various methods have been reported for the preparation of fluorenones such as cyclization of 2-amino diaryl ketones [18] or biaryl carboxylic acids [19], and oxidation of fluorenol [20]. One of the most applicable methods for the synthesis of fluorenones

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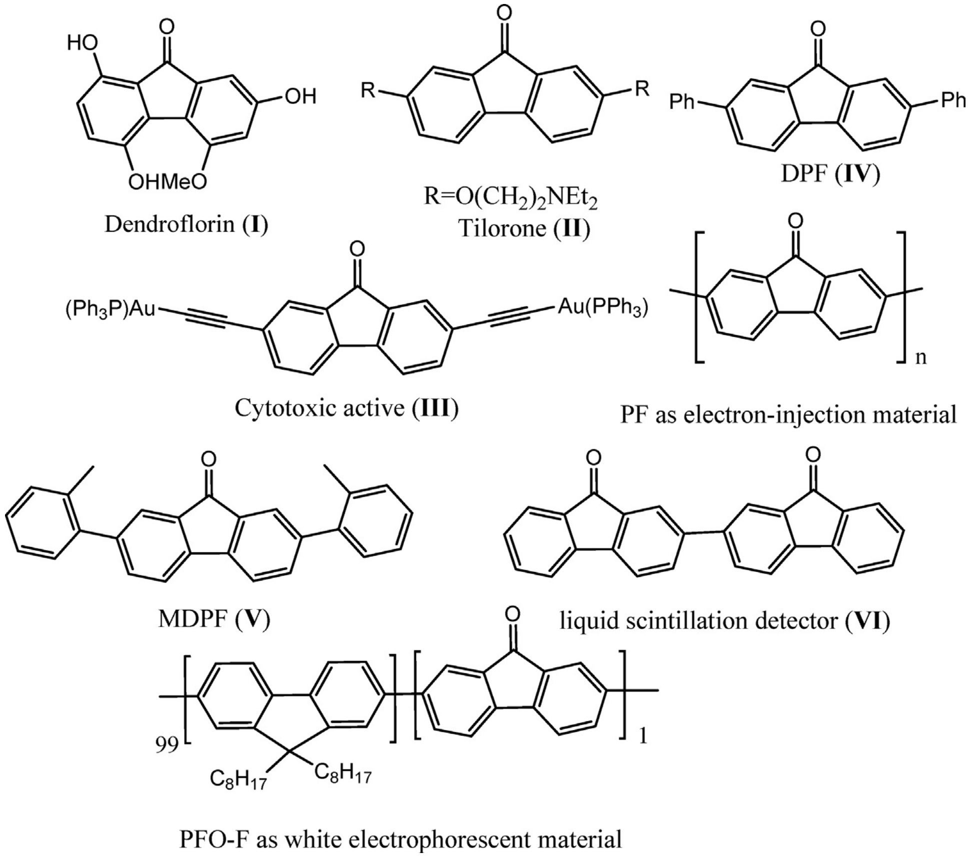


Fig. 1. Representatives of important fluorenones.

is the Pd-catalyzed coupling reactions. In 2016, the synthesis of fluorenone derivatives has reported through Pd-catalyzed ortho-selective oxidative C—H/C—H cross-coupling of aromatic carboxylic acids with arenes and subsequent intramolecular Friedel-Crafts acylation [21]. The synthesis of various substituted fluoren-9-ones has been accomplished by the Pd-catalyzed cyclocarbonylation of o-halobiaryls [22]. Some aryl fluorenones have been synthesized as precursor for the synthesis of biologically and industrially compounds *via* homogeneous Suzuki [11g,16,23] or Sonogashira coupling reaction [24] using 2-bromo or 2,7 dibromo fluorenone. Although there are several synthetic routes to make fluorenones as mentioned above, to the best of our knowledge, employing Pd-based heterogeneous catalyst for the synthesis of fluorenone derivatives has not been previously reported. Herein, for the first time an efficient and reusable heterogeneous catalyst for the synthesis of fluorenones in green solvent medium (ethanol-water) [25] has been reported.

2. Results and discussion

2.1. Synthesis and characterization of Pd@DCA-SBA nanocomposite

The preparation process for the palladium supported SBA-functionalizd 1,2-dicarboxylic acid (Pd@DCA-SBA) nanocomposite is shown in Scheme 1. The SBA-Cl obtained by the reaction of SBA-15 with thionyl chloride. Then, SBA-Cl was reacted with 2-mercaptoethanol to obtain mercaptofunctionalized SBA (SBA-SH) [26]. Subsequently, the reaction of SBA-SH with maleic anhydride followed by hydrolysis leads to the SBA supported 1,2-dicarboxylic groups (SBA-DCA). The final catalyst (Pd@DCA-SBA nanocomposite) was prepared by the reaction of SBA-DCA with an acetonitril solution of palladium acetate at room temperature.

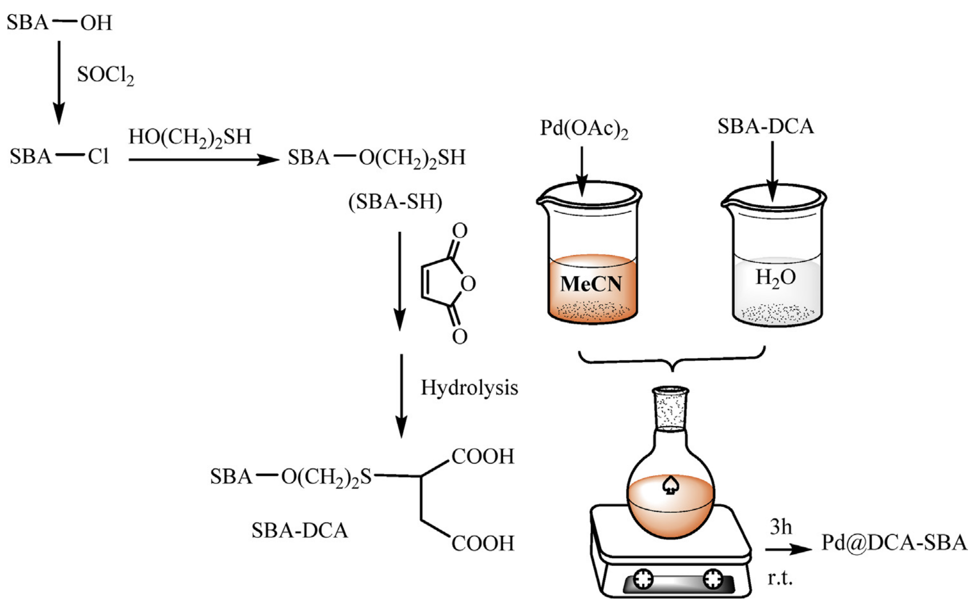
The Pd@DCA-SBA nanocomposite was characterized by FT-IR, TGA, AAS, TEM, and EDS measurements. The FT-IR spectrum of SBA-DCA and Pd@DCA-SBA are shown in Fig. 2. The FT-IR spectrum of SBA-DCA shows a characteristic band at 1656 cm^{-1} ascribe to C=O of carboxylic acid groups. This clearly confirms the functionalization of SBA by 1,2-bidentate carboxyl groups. The C=O bands of Pd@DCA-SBA were shifted to a lower frequency in the IR spectrum (1627 cm^{-1}) due to the formation of a metal–ligand bond [27].

Thermogravimetric analysis (TGA) was further used to study the composition of the Pd@DCA-SBA nanocomposite (Fig. 3). TGA plot of catalyst shows a weight loss at ~100 °C and was assigned to adsorbed water. The 8.3% weight loss at above ~220 °C (and continuing to ~600 °C) is related to the decomposition of covalently bonded organic groups from the Pd@DCA-SBA. It shows that the catalyst has good thermal stability until 220 °C. The palladium content of Pd@DCA-SBA nanocomposite was calculated (0.5 mmol g^{-1}) by AAS.

The morphology of fresh SBA-15 and Pd@DCA-SBA nanocomposite were determined by transmission electron microscopy (TEM). The Fig. 4a shows the porous structure of fresh SBA-15. A good distribution of palladium nanoparticles with average particle size of 12–15 nm is illustrated in Fig. 4b,c and indicates no change in the porous structure of the support and also no detectable aggregation of Pd nanoparticles. The energy dispersive X-ray spectroscopy (EDS) of Pd@DCA-SBA nanocomposite also clearly shows the presence of elements Pd, C, O and S in the composite (Fig. 5).

2.2. The catalytic activity of the catalyst

For fluorenones synthesis, the catalytic activity of Pd@DCA-SBA nanocomposite was investigated in the Suzuki-Miyaura cross coupling reaction of 2-bromo fluorenone **1** and aryl bronic acids **2**. The



Scheme 1. The schematic diagram of catalyst preparation.

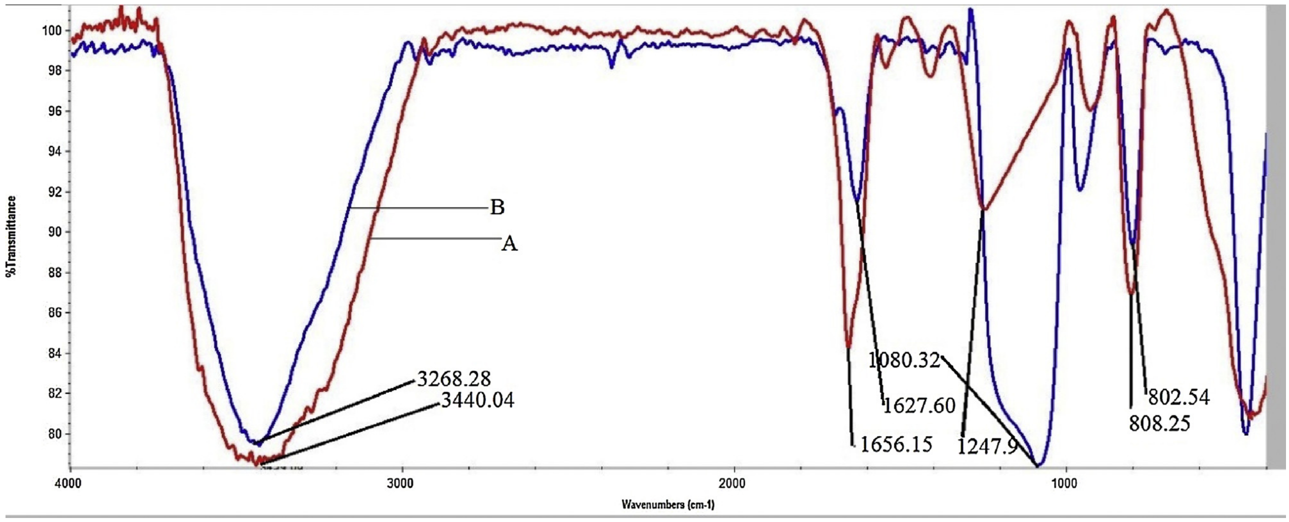


Fig. 2. FT-IR spectra of SBA-DCA (A) and Pd@DCA-SBA (B).

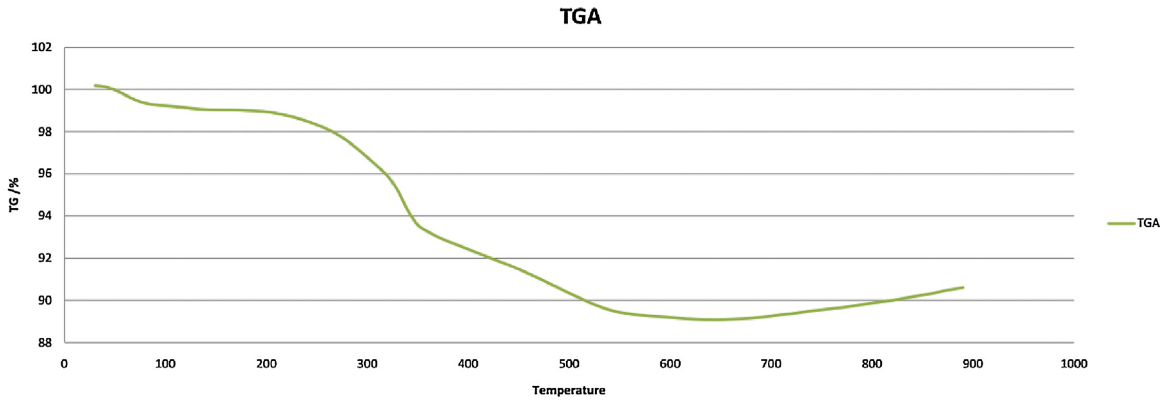


Fig. 3. TGA of Pd@DCA-SBA nanocomposite.

coupling reaction of 2-bromo fluorenone **1a** and phenyl boronic acid **2a** was chosen as model reaction in different conditions. By using K_2CO_3 as base and in the presence of 0.2 mol% catalyst, the reaction was tested employing various solvents such as H_2O, MeOH, EtOH, H_2O-EtOH, and toluene at 80 °C (Table 1, entries 1–5). A superior yield was obtained when H_2O-EtOH (1:1) was used as

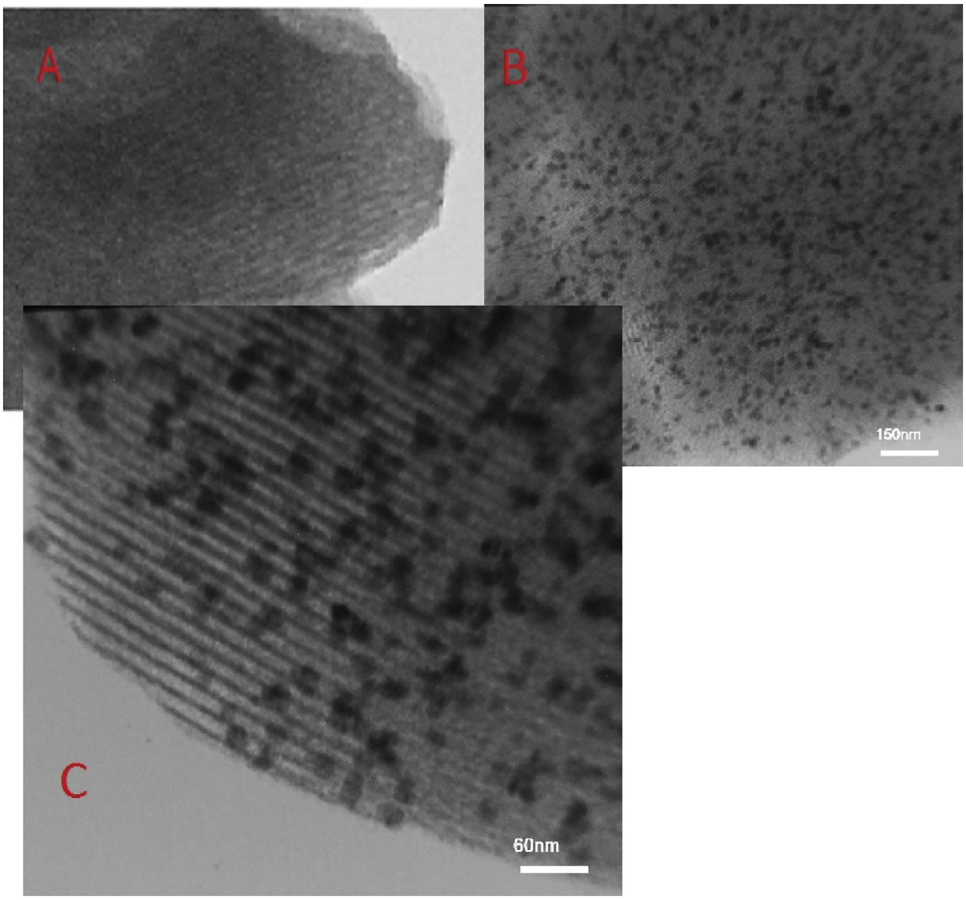


Fig. 4. TEM image of fresh SBA-15 (A) and Pd@DCA-SBA nanocomposite (B, C).

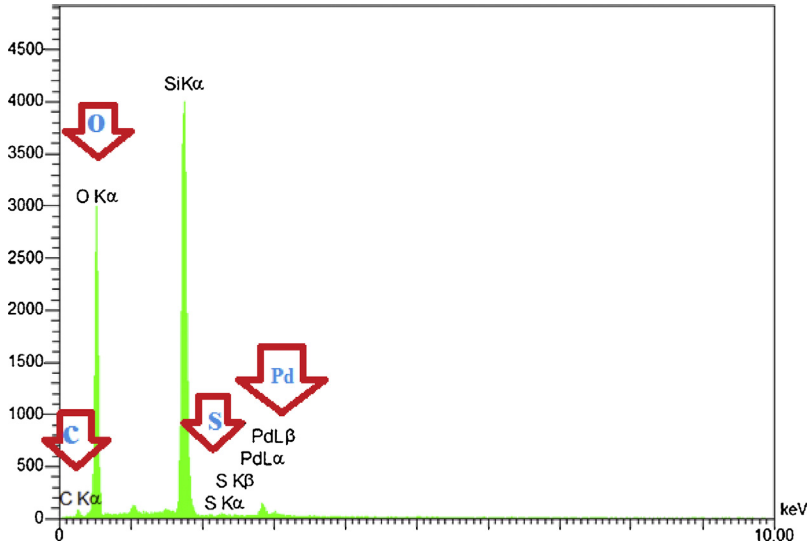
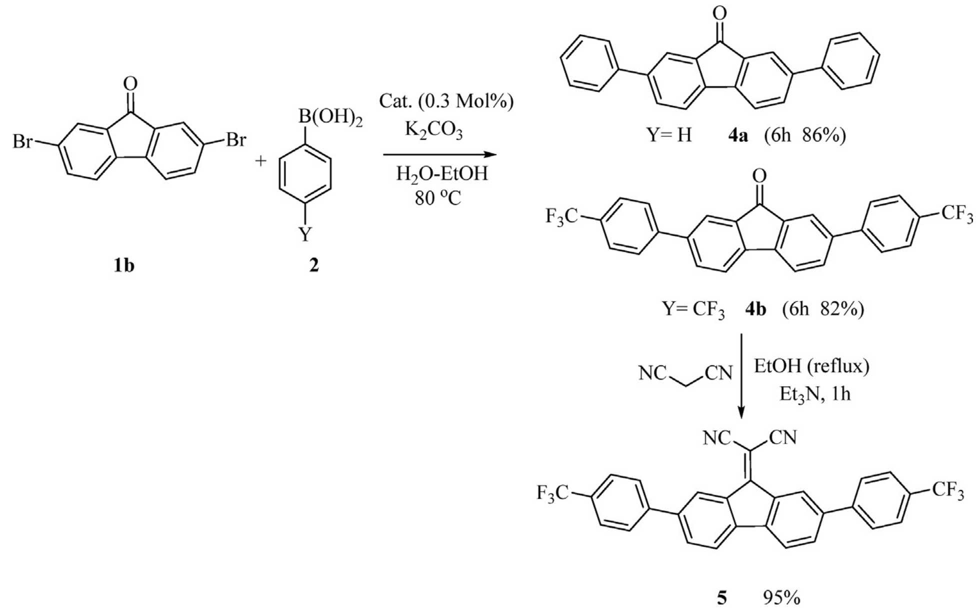


Fig. 5. Energy dispersive X-ray spectroscopy (EDS) of Pd@DCA-SBA.

the solvent (Table, Entry 5). Then, different bases were screened in the model reaction. The reaction did not proceed in the presence of $NaHCO_3$ and moderate yield was obtained with Cs_2CO_3 and KOtBu (Table 1, Entry 6–8). Also, some experiments were carried out in different temperature and 80 °C was the optimum reaction temperature (Table 1, Entries 5, 9 and 10). The effect of amount of Pd@DCA-SBA was also investigated under the optimum reaction conditions (Entries 5, 11 and 12). It was found that when the amount of catalyst increased from 0.1 and 0.2 to 0.3 mol%, the yield increased from 71% and 85%, and 86%, respectively. It was found that 0.2 mol% Pd@DCA-SBA is sufficient to push this reaction forward (Table 1, entry 5). Then, the effect of dicarboxylic acid groups in the catalyst was investigated. The palladium supported on SBA-15 as an unmodified SBA-15 catalyst was synthesized and tested in the model reaction in optimum reaction conditions. As can be seen in Table 1, the yield of product was 62% (Entry 13). According to the



Scheme 2. Synthesis of 2,7-diaryl fluorenones.

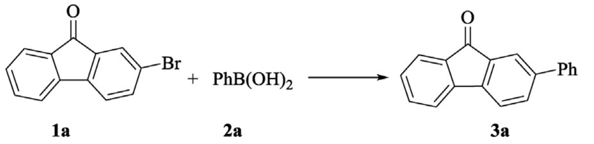
result, the dicarboxylic acid groups make higher catalytic activity for the reaction.

After optimization of the reaction conditions, we screened various boronic acids to explore the scope of the reaction (Table 2). The catalyst showed good reactivity and the reaction was performed with good to excellent yield with boronic acids containing both electron donating and electron withdrawing functionalities.

The catalyst was even effective for synthesis of 2,7-diaryl fluorenones **4** by Suzuki reaction of two sites of 2,7-dibromo fluorenones **1b** with boronic acids **2** using 0.3 mol% catalyst (Scheme 2). The compound **5** has been synthesized via homogeneous Pd-catalyst and reported as potential material in organic electroluminescence systems [30]. As shown in Scheme 2, the catalyst was successfully applied to prepare compound **5** through a Suzuki cross-coupling and subsequently Knoevenagel condensation with malononitrile.

Encouraged by this success, we examined the catalytic activity of Pd@DCA-SBA nanocomposite in Ullmann homocoupling reaction of 2-bromo fluorenone **1a** in the presence of 0.2 mol% of catalyst. After optimization of reaction conditions, the 9H,9′H-[2,2′-bifluorene]-9,9′-dione **6** was obtained in 60% yield in the presence of glucose as a reducing agent [31] (Scheme 3).

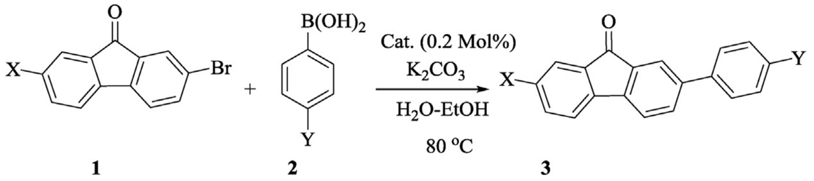
Table 1
Screening of the reaction conditions[a].



Entry	Solvent	Catalyst (mol%)	Base	T (°C)	Yield[b] (%)
1	H_2O	0.2	K_2CO_3	80	52
2	EtOH	0.2	K_2CO_3	80	65
3	MeOH	0.2	K_2CO_3	80	32
4	Toluene	0.2	K_2CO_3	80	48
5	H_2O-EtOH (1:1)	0.2	K_2CO_3	80	85
6	H_2O-EtOH (1:1)	0.2	KO^tBu	80	64
7	H_2O-EtOH (1:1)	0.2	Cs_2CO_3	80	75
8	H_2O-EtOH (1:1)	0.2	$NaHCO_3$	80	<20
9	H_2O-EtOH (1:1)	0.2	K_2CO_3	60	71
10	H_2O-EtOH (1:1)	0.2	K_2CO_3	90	83
11	H_2O-EtOH (1:1)	0.3	K_2CO_3	80	86
12	H_2O-EtOH (1:1)	10.	K_2CO_3	80	71
13[c]	H_2O-EtOH (1:1)	0.2	K_2CO_3	80	62

[a] phenylboronic acids (1.2 mmol), 2-bromo fluorenone (1 mmol), base (2 mmol).
[b] Isolated yield.
[c] Catalyst = Pd@SBA.

Table 2
Synthesis of fluorenones by the Suzuki reaction.



Product **3**	X	Y	Time (h)	Yield (%)[a]	M.P. (°C)	Ref.
a	H	H	1.5	85	141–142	[28]
b	H	OMe	2	83	138–139	[23a]
c	H	Me	2	84	140–142	[29]
d	H	CF_3	1.5	85	177–178	–
e	Br	H	3	84	209–211	[23c]
f	Br	OMe	2	85	211–212	–

[a] Isolated Yield.

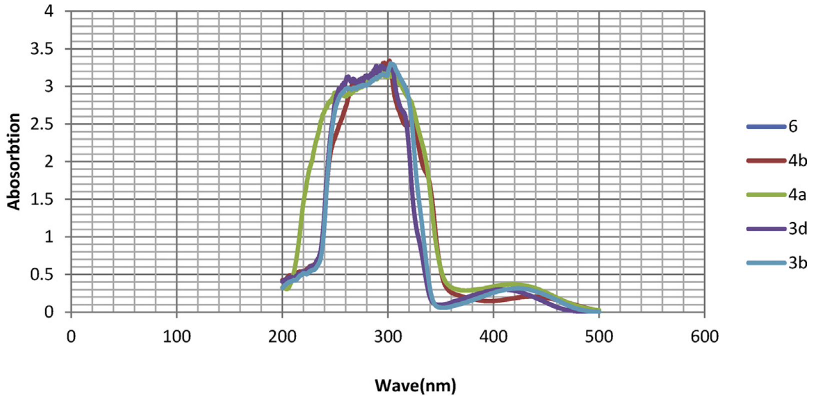
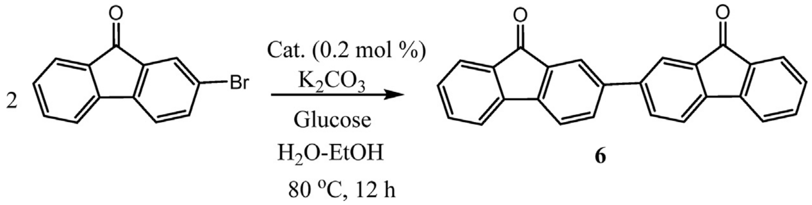
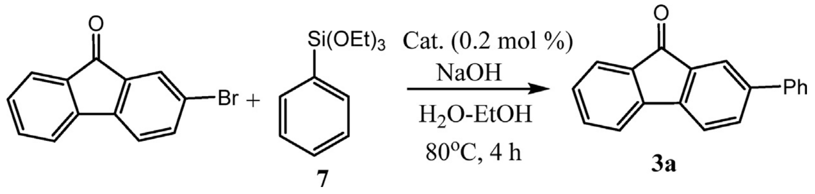


Fig. 6. The UV/Vis spectra of selected compounds.



Scheme 3. Synthesis of 9H,9′H-[2,2′-bifluorene]-9,9′-dione **6**.



Scheme 4. The Hiyama cross-coupling reaction for the synthesis of 2-phenyl fluorenone **3a**.

Table 3
Photophysical data for absorption (abs) and fluorescence (flu) of selected products in $CHCl_3$.

Compound	log ε	$\lambda_{abs,max}$/nm	$\lambda_{flu,max}$/nm
3b	3.26	306	570
3d	3.28	203	560
4a	3.21	296	570
4b	3.30	302	560
6	3.17	296	570

To the best of our knowledge, synthesis of fluorenone derivatives via Hiyama cross-coupling reaction has not been previously reported. Therefore, the application of the Pd@DCA-SBA catalyst in Hiyama cross-coupling reaction of triethoxy(phenyl)silane **7** and 2-bromo fluorenone **1a** was tested at the same reaction conditions (0.2 mol% cat., K_2CO_3) and corresponding product **3a** was obtained in 42% yield after 4 h. It was found that increasing amounts of the catalyst and reaction time did not improve the yield. A review to the literatures revealed us that NaOH is good choice as the base [32]. Consequently, we checked the reaction in H_2O-EtOH using NaOH in the presence of 0.2 mol% of catalyst and product **3a** was obtained in 65% yield (Scheme 4).

Electronic absorption and fluorescence spectra of 2×10^{-5} M solutions of selected products 3, 4 and 6 in $CHCl_3$ were measured and the results are shown in Table 3 and Figs. 6 and 7. All selected compounds showed strong absorptions, with maximum wavelengths in the range of 296–306 nm (Fig. 6). Fig. 7 shows the emission spectra of selected products. From Fig. 7, it can be observed that the products are fluorescent in solution and their λ_{flu} are at green light (560–570 nm). The λ_{flu} are presented in Table 3.

The observation of great potential activity of the catalyst in Suzuki coupling reaction of aryl boronic acids and bromo fluorenones encouraged us to investigate the activity of catalyst in Suzuki reaction for biaryl synthesis. As can be seen from Table 4, the Suzuki coupling of aryl iodides and bromides **8** with aryl boronic acids **2** in the presence of 0.2 mol% of the catalyst using K_2CO_3 as a base in H_2O-EtOH at 80 °C afforded biaryl derivatives **9** in excellent yields. Under the same reaction conditions the coupling of chlorobenzene provided the target product in good yields.

The catalyst was even effective for the synthesis of teiphenyl **11** by the reaction of 2,4-dilodo benzene **10** including two sites with boronic acids **2** (Scheme 5).

Then, we examined the heterogeneous nature of the catalyst. First, we performed a mercury poisoning test by entering an excess amount of Hg in the Suzuki reaction of phenylboronic acid and 2-bromo fluorenone **1a**. The reaction yield fell down in the presence of mercury due to the amalgamation with PdNPs. The results confirm us the heterogeneous nature of the catalyst, more over it can be concluded that Suzuki reaction proceeded via Pd(0)/Pd(+2) mechanism [33]. In the next step, to assess the palladium leaching from the catalyst during the reaction we performed the hot filtration test for Suzuki reaction of 2-bromo fluorenone **1a** and phenylboronic acid. The reaction was stopped after ~50% of the reaction. The hot filtrates were then transferred to another flask containing base and H_2O-EtOH at 80 °C. Upon further heating of the catalyst-free solution for 7 h, no considerable progress (~6% by GC analysis) was observed. Moreover, using AAS of the same reaction solution at the

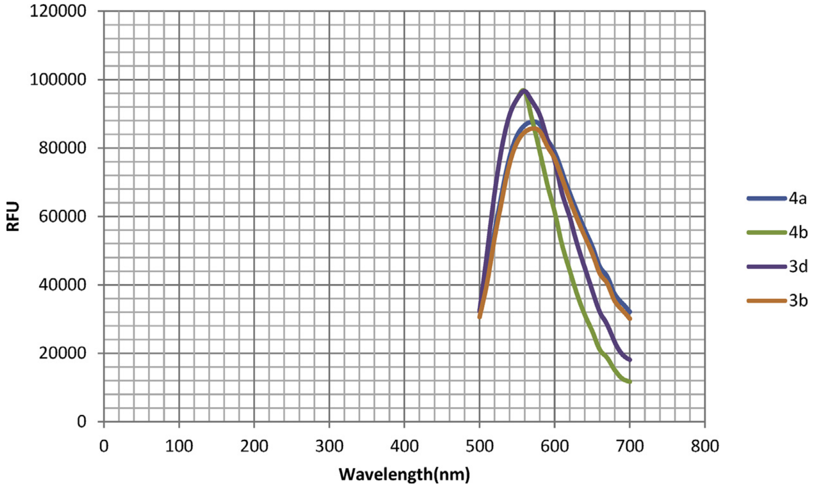
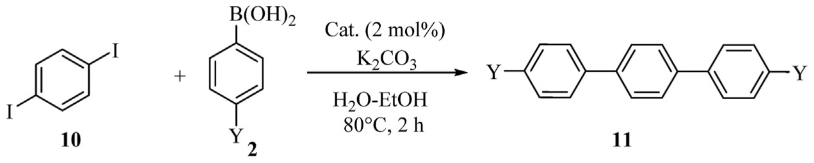


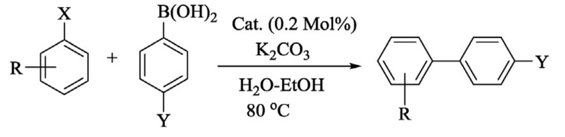
Fig. 7. The fluorescence spectra of selected compounds.



Y= H (**11a**, 94 %), OMe (**11b**, 90 %)

Scheme 5. Suzuki reaction of aryl boronic acids with 2,4-diiodo benzene.

Table 4
Suzuki reaction for the biaryl synthesis.



8 **2** **9**

Product **5**	Y	X	R	Time (h)	Yield (%)
a	H	I	H	2	95
b	H	I	4-Me	2	94
c	H	I	4-OMe	2	95
d	4-OMe	I	H	2	95
e	H	I	4-COMe	4	95
f	H	I	2-Me	2	94
g	H	Br	H	2	95
h	H	Br	4-NO_2	2	92
i	4-OMe	Br	4-NO_2	2	93
j	H	Br	4-Me	2	95
K	4-Me	Br	4-Me	2	94
M	H	Cl	4-NO_2	8	78
N	4-OMe	Cl	4-NO_2	8	80
O	4-Me	Cl	H	8	79
P	H	Cl	H	8	76

[a] Isolated yield.

midpoint of completion indicated that no significant quantities of palladium are lost to the reaction liquors during the process. The reusability of the catalyst was also investigated in the Suzuki coupling reaction of phenylboronic acid with three haloarenes, phenyl iodide, 2-bromo fluorenone and phenyl chloride. As can be seen in Fig. 8, the catalyst could be reused successively at least five times without significant loss of activity. All results confirm the reaction occurs mainly via a heterogeneous pathway. In addition, as shown in Fig. 9, no detectable aggregation for palladium NPs was observed in the recovered Pd@DCA-SBA nanocomposite after 5 runs.

3. Experimental

3.1. *Preparation of SBA-Cl [26]*

Thionyl chloride (8 mL) was added to 1 g of oven dried SBA-15 (120 °C, vacuum) in a round bottomed flask equipped with a condenser and a drying tube and refluxed for 48 h. Excess of thionyl chloride was distilled off and the resulting product was flame-dried and stored in a sealed vessel. This silica chloride can be used for months without losing its activity.

3.2. *Preparation of SBA-SH*

2-Mercaptoethanol (3 mL) was added to 1 g SBA-Cl and was stirred vigorously for 24 h at room temperature. Then the mixture was filtered and washed with ethanol, acetone, and water.

3.3. *Preparation of SBA-DCA [27]*

SBA-15–SH (2.0 g) and maleic anhydride (1.96 g, 20 mmol) in 50 mL of THF was stirred at room temperature under argon atmosphere. After 1 h, triethylamine (5 mmol) was added and stirred for 24 h. The products were collected by centrifugation and washed with water. Then, the product was stirred in deionized water at 80 °C for 24 h for dicarboxyl groups formation. Finally, the products were washed with water, ethanol and acetone and dried.

3.4. *Preparation of Pd@DCA-SBA nanocomposite*

The SBA-DCA (0.5 g) was ultrasonically dispersed in 5 mL of deionized water. Then, a solution of $Pd(OAc)_2$ (0.2 g) in acetonitrile was added and the mixture was stirred for 10 h. After filtration and washing with deionized water, acetonitrile and ethanol the final material was dried at 70 °C for 12 h. The Pd concentration in the Pd@DCA-SBA was determined by atomic adsorption spectroscopy

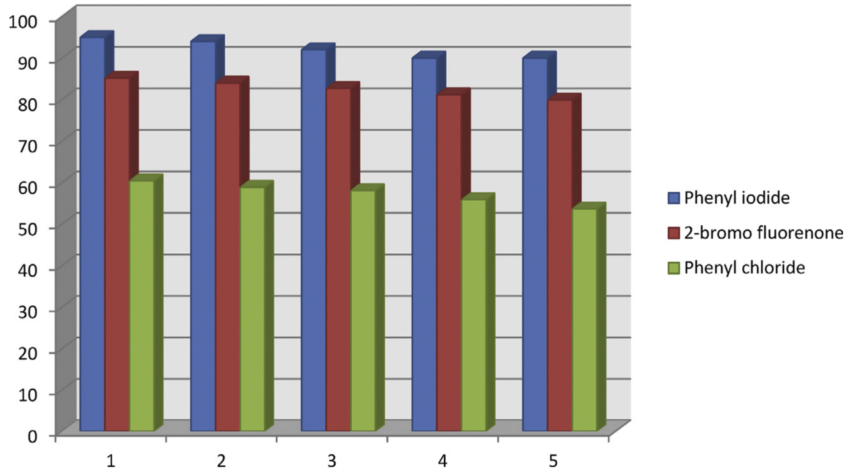


Fig. 8. The reusability of the catalyst in the Suzuki reaction of phenylboronic acid with phenyl iodide, 2-bromo fluorenone and phenyl chloride.

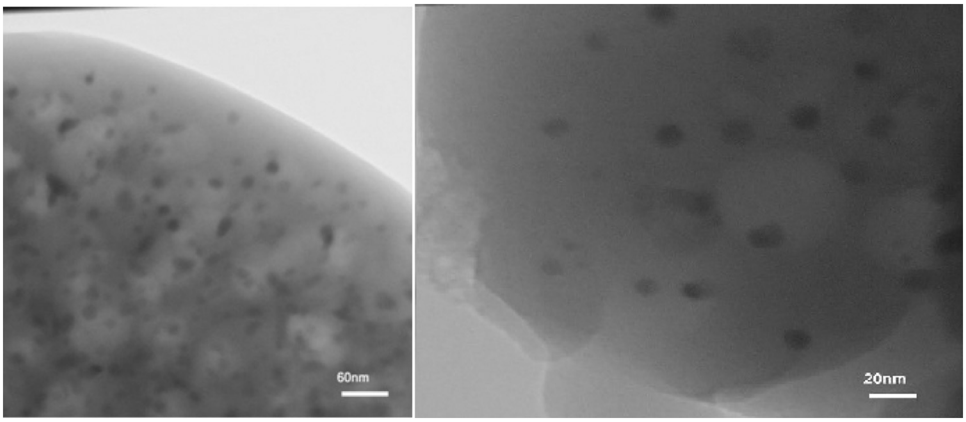


Fig. 9. TEM image of Pd@DCA-SBA nanocomposite after 5 reaction cycles.

(AAS) following digestion with concentrated aqua regia solution at 80 °C, and was found to be 0.5 mmol g^{-1}

3.5. *General procedure for Suzuki reaction of 9-fluorenone*

A mixture of Pd@DCA –SBA (0.2 mol% of Pd), K_2CO_3 (2 mmol), 9-fluorenone (1.0 mmol), aryl boronic acid (1.2 mmol) in H_2O-EtOH (3 mL, 1:1) was stirred at 80 °C for appropriate time (Table 2). After completion of the reaction, the catalyst was separated and the filtrate was extracted with ethyl acetate (2 × 5 mL). The organic solvents were removed under vacuum and the product **3** was purified by recrystalization.

3.6. *General procedure for the synthesis of bisfluorenone*

A mixture of Pd@DCA-SBA (0.2 mol% of Pd), K_2CO_3 (2 mmol), 9-fluorenone (1.0 mmol), glucose (1 mmol) in H_2O-EtOH (3 mL, 1:1) was stirred at 80 °C for 12 h at 80 °C. After completion of the reaction, the catalyst was separated and the filtrate was extracted with ethyl acetate (2 × 5 mL). The organic solvents were removed under vacuum and the product **3** was purified by preparative TLC (*n*-Hexane).

3.7. *General procedure for the Hiyama reaction of 9-fluorenone*

A mixture of Pd@DCA-SBA (0.2 mol% of Pd), NaOH (2 mmol), 9-fluorenone (1.0 mmol), triethoxyphenylsilane (1.0 mmol), in H_2O-EtOH (3 mL, 1:1) was stirred at 80 °C for 4 h. After completion of the reaction, the catalyst was separated and the filtrate was extracted with ethyl acetate (2 × 5 mL). The organic solvents were removed under vacuum and the product **3** was purified by preparative TLC (*n*-Hexane).

3.8. *General procedure for the Biaryl synthesis via Suzuki reaction*

A mixture of Pd@DCA-SBA (0.2 mol% of Pd), K_2CO_3 (2 mmol), aryl halide (1.0 mmol), and aryl boronic acid (1.2 mmol) in H_2O-EtOH (3 mL, 1:1) was stirred at 80 °C for appropriate time (Table 3). After completion of the reaction, the catalyst was separated and the filtrate was extracted with ethyl acetate (2 × 5 mL). The organic solvents were removed under vacuum and the product **9** was purified by preparative TLC (*n*-Hexane).

4. Conclusions

We have demonstrated for the first time that Pd@DCA-SBA nanocomposite is an effective and powerful heterogeneous catalyst for the synthesis of fluorenone derivatives by homo and cross coupling reactions in H_2O-EtOH as green solvent. In addition, the negligible leaching of palladium from catalyst was proved by AAs and the catalyst was recovered by simple filtration and reused for several cycles without a significant loss of catalytic activity. Furthermore, the TEM image of the recovered catalyst showed the presence of well-distributed Pd NPs on the catalyst without any aggregation. Further applications of the catalytic system in other palladium catalyzed reactions are under investigation in our laboratory.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2017.12.035.

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