A facile synthesis of PdCo bimetallic hollow nanospheres and their application to Sonogashira reaction in aqueous media

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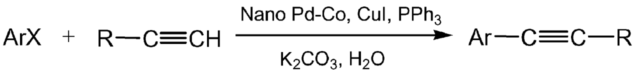
PdCo bimetallic hollow nanospheres with a diameter of about 80 nm were for the first time synthesized in polyethylene glycol solution. This new Pd-containing bimetallic hollow nanostructure was successfully applied to catalysis of the Sonogashira reaction, which reveals obvious advantages such as environmentally friendly reaction conditions (the reaction proceeded in water), the recyclability of the catalyst, simple experimental operation and high yields.

As an important route for the synthesis of aryl alkynes by the coupling of terminal alkynes and aryl halides, the Sonogashira reaction has always aroused the interest of chemists.[1] This method has been applied for the synthesis of natural products, bioactive compounds and materials.[2] Numerous palladium-complexes have been employed to catalyze this transformation in recent years. It is thought that the basic ligands in the complexes designed to provide the requisite electron density on palladium in order to achieve oxidative addition of Pd to aryl halides indeed facilitate successful coupling reactions.[3] The reaction generally proceeds in organic solvents such as amines, benzene, THF, DMF *etc.* in which the catalyst can dissolve to form a homogeneous system. These soluble palladium reagents tend to be expensive and sometimes difficult to manipulate and recover. Moreover, the reactions are generally air-sensitive and the solvents also pose recyclability (waste handling) problems of their own. In addition, amines such as piperidine, diethylamine and triethylamine are required in most Sonogashira reactions and they add to the environmental burden. Thus, it is essential to develop new Pd-based catalysts and reaction media to overcome these problems.

In recent years, there has been growing interest in the fabrication of Pd nanoparticles and their applications in organic reactions especially the formation of carbon–carbon bonds.[4] For example, ligand-free Pd nanoparticles of about 3.3 nm in size stabilized by tetraalkylammonium salts bearing long alkyl chains were obtained and used as heterogeneous catalyst for the Suzuki and Stille cross-coupling reactions of aryl halides carried out in ionic liquids.[5] Palladium hollow spheres with diameters of about 300 nm were prepared by using silica spheres as templates, and these showed good catalytic activities in Suzuki coupling reactions and could be reused several times by simple filtering and retrieving without loss of catalytic activity.[6] The high surface area of the hollow spheres resulting from the nanoparticulate nature of the shell, which is much larger than that of dense spheres of the same diameter, is responsible for the high catalytic activity. Generally, this kind of "hard template" method can ensure relatively good control over the morphology of the final products and thus allows one to obtain a hollow nanostructure, but the addition and then removal of the templates may complicate the synthetic procedures and limit the scale on which a material can be synthesized. Therefore, direct solution-phase approaches to Pd-containing hollow spheres need to be explored. On the other hand, in order to reduce the cost of Pd catalysts and/or raise their utilization efficiency, bimetallic nanoparticles can be used. Hyeon and co-workers synthesized Pd/Ni bimetallic nanoparticles with a cheap metal core (Ni) and a noble metal shell (Pd), which can be used in Sonogashira coupling reactions. The toxic organic solvent diisopropylamine (DIA) or toluene, however, should be used for this reaction.[7]

To date, only a few examples of Pd-containing bimetallic hollow nanospheres exist in the literature.[8] Furthermore, there is no report of the use of such materials as catalysts in C–C bond forming processes in aqueous solution. In this communication, PdCo bimetallic hollow spheres of about 80 nm diameter were for the first time synthesized using a solution-phase approach. These new bimetallic hollow nanospheres were then successfully applied as catalysts in the Sonogashira reaction. The reaction was carried out in water and good to excellent yields were achieved (Scheme 1).

Fig. 1 shows the XRD pattern of the sample prepared by the redox reaction of $CoSO_4$ and H_2PdCl_4 with $NaBH_4$ in 0.25 g mL^{-1} polyethylene glycol solution. The diffraction peaks in the range of $10 \leqslant 2\theta \leqslant 70°$ can be indexed as cubic Pd (111), (220), and hexagonal Co (002), (101), which are in good accordance with ASTM standard 5-681 (Pd) and 5-727 (Co), respectively, and mean that the sample is composed of metallic Pd and Co instead of their alloy. The peaks are fairly broad, even overlapping with neighbors, indicating the small particle size. A rough estimation employing Scherrer's equation indicates the size of the particles forming the PdCo hollow spheres is about 4.0 nm.[9] Fig. 2 gives the energy-dispersive spectrometry (EDS) analysis of the sample. The results



$$\mathrm{ArX} + \mathrm{R{-}C{\equiv}CH} \xrightarrow[\mathrm{K_2CO_3,\ H_2O}]{\text{Nano Pd-Co, CuI, PPh}_3} \mathrm{Ar{-}C{\equiv}C{-}R}$$

Scheme 1

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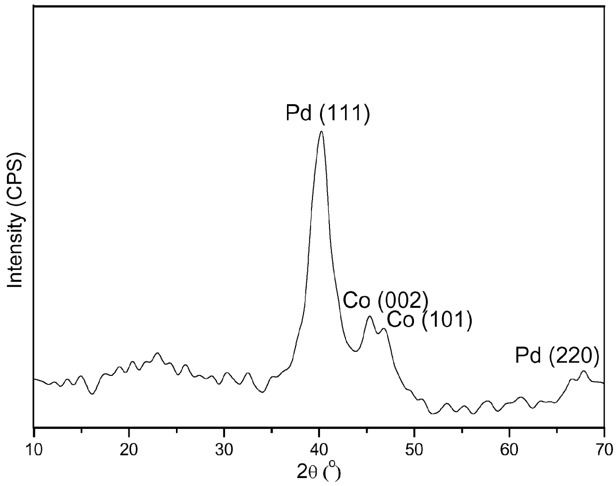

Fig. 1 XRD pattern of PdCo bimetallic hollow nanospheres.

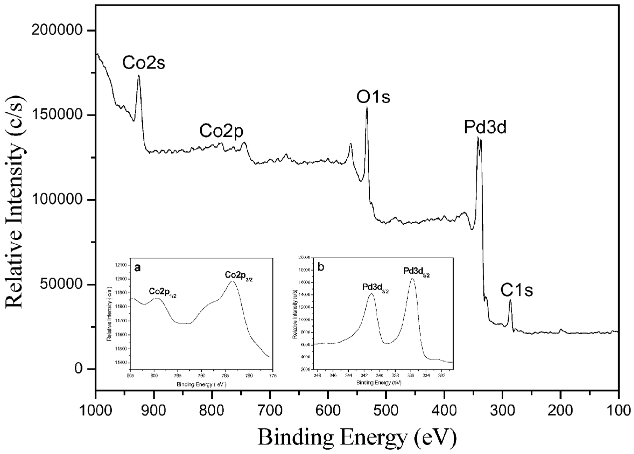

Fig. 3 XPS spectra of the PdCo bimetallic hollow nanospheres. The insets a and b show the magnified analysis of the Co2p and Pd3d peaks, respectively.

demonstrate the coexistence of Pd and Co with an atom ratio of 3.5 : 1. Also, carbon and oxygen were found in the EDS analysis, meaning a small amount of polyethylene glycol existed in the sample. Further evidence comes from the FTIR spectra, which show the absorption peaks of the polyethylene glycol (not shown here). Fig. 3 shows the XPS spectra of the sample. It can be seen from the figure that the sample is composed of Pd, Co, C and O elements. The binding energies of Pd(3d$_{5/2}$) and Pd(3d$_{3/2}$) are 335.9 and 341.0 eV (Inset b of Fig. 3), respectively, which are similar to those reported for Pd metal in the literature.[10] However there is a small chemical shift toward higher binding energies for Co2p$_{3/2}$ (783.5 eV) and Co2p$_{1/2}$ (799.4 eV) (Inset a of Fig. 2) as compared to metallic Co,[11] implying that the Co on the surface of the PdCo particles is being oxidized. In addition, the C1s and O1s peaks in Fig. 3 can be attributed to the polyethylene glycol, which is in accordance with the EDS analysis. A typical TEM image of the sample is shown in Fig. 4a. From the TEM image, we can see pale regions in the central parts in contrast to the dark edges, implying hollow spherical structures. The same contrast difference between the center and edge in the TEM images of one sphere is obtained when the sample grid is rotated by different degrees and this further proves their hollow structures. The corresponding selected area electron diffraction pattern of the hollow nanospheres shown in the inset of Fig. 4a shows regular diffraction rings, indicating that the hollow nanospheres are composed of polycrystals. Those diffraction rings can be indexed to cubic Pd (220), (420), and hexagonal Co (103), (220), further confirming the formation of a bimetallic nanostructure. The average diameter of the hollow spheres is about 80 nm with most of them in the range 60 to 90 nm. The high-resolution TEM (HRTEM) image of the sample shown in Fig. 4b reveals that the shell wall is composed of primary PdCo nanoparticles with an average diameter of about 3.5 nm, and that the shell thickness is about 9 nm. To the best of our knowledge, this is the first example of hollow Pd-containing bimetallic nanospheres prepared by using the direct solution-phase approach.

It is necessary to point out that PdCo hollow nanospheres can be easily obtained in high yields up to 70% by using present method. The polyethylene glycol plays an important role in the formation of the hollow spheres. When the experiment was carried out in the absence of polyethylene glycol, the

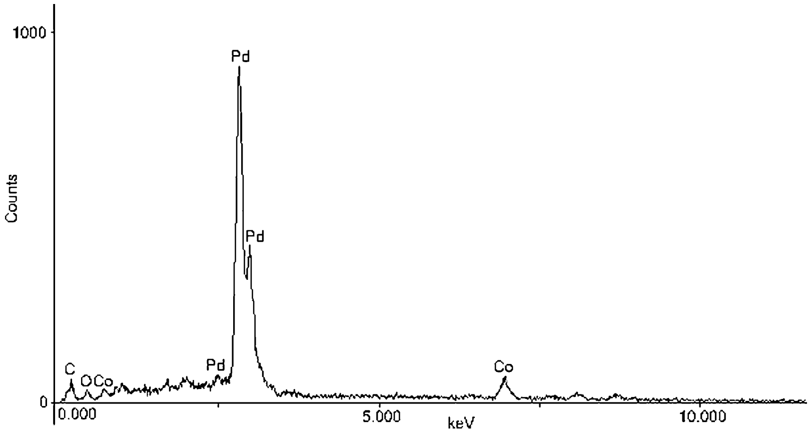

Fig. 2 EDS of PdCo bimetallic hollow nanospheres.

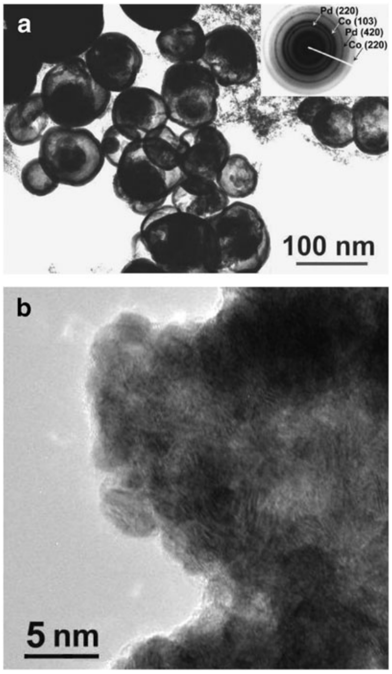

Fig. 4 (a) TEM and (b) high-resolution TEM images of PdCo bimetallic hollow nanospheres.

products were solid PdCo particles of about 40 nm in size (Fig. 5). In addition, solid Pd particles, instead of hollow spheres, of about 30 nm were obtained when the reaction was carried out in the same conditions but without $CoSO_4$. Contrarily, in the absence of H_2PdCl_4 but keeping the other conditions constant, Co hollow spheres with an average diameter of about 80 nm were formed. These facts mean that cobalt ions also play an important role in the formation of the PdCo bimetallic hollow spheres. The polyethylene glycol chain contains many hydrophilic and hydrophobic sites and has a high degree of flexibility in that the C–O bond is easily rotated, and can form various conformations such as extended chains or coils under different conditions. We speculate that the formation of the PdCo hollow spheres might result from polyethylene glycol spherical aggregates formed mainly *via* the affinity of the oxygen atoms of the polyethylene glycol for Co^{2+} ions. In such aggregates, the hydrophobic hydrocarbon chains of the polyethylene glycol are oriented toward the interior of the aggregates, while the $[PdCl_4]^{2-}$ (the pH of the solution being 7–8) and Co^{2+} ions are mainly located on the surface of the aggregates to form a Co- and Pd-containing coating which creates a nucleation domain of Co and Pd for the subsequent redox reaction. As the redox reaction proceeds, a metallic shell is formed on the surface of the aggregates. The reason that pure Pd hollow spheres failed to form might be that the polyethylene glycol spherical aggregates can not form in the H_2PdCl_4–polyethylene glycol solution because there is no complexation of $[PdCl_4]^{2-}$ ions with the oxygen atoms of the polyethylene glycol. Similar spherical aggregates have also been observed in a solution of $Cd(OAc)_2$ and polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) in THF due to the complexation of Cd^{2+} ions with the 2-vinylpyridine units,[12] and in an aqueous solution of $Cd(OAc)_2$ and the triblock copolymer poly(ethylene oxide)poly(propylene oxide)poly(ethylene oxide) (EO_{20}-$PO_{70}EO_{20}$) *via* the complexation of Cd^{2+} ions with the EO and PO units.[13] Further evidence comes from the FTIR (Fig. 6). It reveals that although most of the IR spectrum of H_2PdCl_4- (Fig. 6b) or $CoSO_4$- (Fig. 6c) containing polyethylene glycol aqueous solution is similar to that of pure polyethylene glycol aqueous solution (Fig. 6a), but there is a change in the case of $CoSO_4$-containing solution in that the vibration of the C–O–C is shifted to higher wavenumber from 1092 cm^{-1} to 1106 cm^{-1}. This results from the covalent properties increasing with the partial donation of the oxygen atom lone pair electrons to the vacant d-orbitals of the Co^{2+} ions. This means that the coordination of the oxygen atoms in the polyethylene glycol with Co^{2+} ions does indeed exist and plays a key role in the formation of the polyethylene glycol spherical aggregates and PdCo bimetallic hollow spheres. The details of the mechanism of formation need further investigation. As to the polyethylene glycol contained in the nanospheres, it can be removed from the shells upon washing.[13]

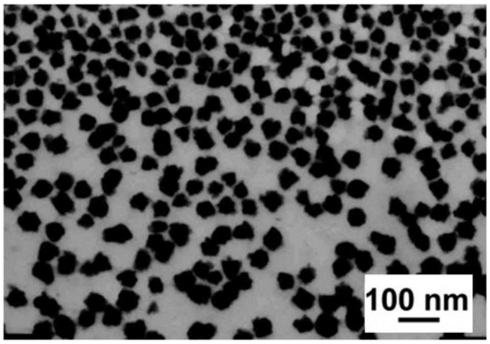

Fig. 5 TEM images of PdCo bimetallic solid nanoparticles.

PdCo bimetallic hollow nanospheres were successfully used to catalyze the Sonogashira reaction. The reaction conditions were first studied. The coupling of phenylacetylene and

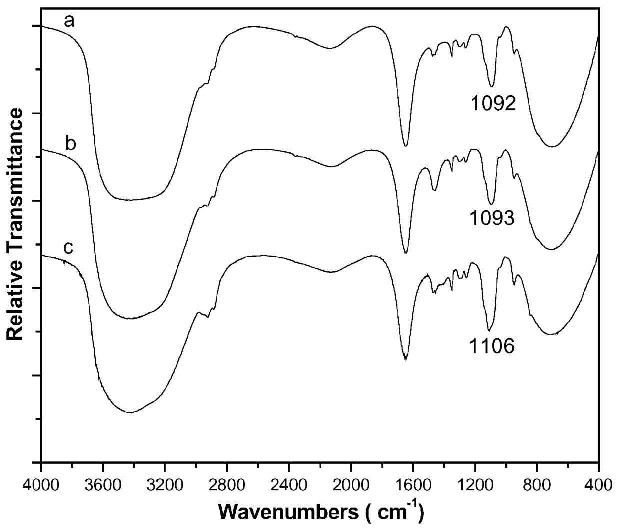

Fig. 6 (a) FTIR spectrum of the pure polyethylene glycol aqueous solution; (b) and (c) FTIR spectra of H_2PdCl_4- and $CoSO_4$-containing polyethylene glycol aqueous solution, respectively.

p-iodotoluene was chosen as a model reaction for the investigation. Solvents such as THF, acetonitrile, DMF, isopropanol, isopropanol–H_2O, H_2O were employed as reaction media. The results showed that under basic conditions (K_2CO_3), in the presence of a nanopalladium–cobalt catalyst, CuI and PPh_3, all of the above systems gave the coupling product with moderate to good yields after 6 h at 70–80 °C. In water, the yield (87%) was lower than that in isopropanol (95%), and similar to that in isopropanol–H_2O (90%) and THF (85%). However in DMF and acetonitrile, the reaction gave only moderate yields (80% and 70%, respectively). Considering that water is an environmentally friendly solvent, it was chosen as the solvent for this reaction. The experiment indicated that 5 mol% of catalyst (that is, about 3.9 mol% of Pd) was sufficient to catalyze the reaction. As co-catalyst and ligand, cuprous iodide and triphenylphosphine were essential to the reaction. Without them, the reaction gave only traces of product. A basic environment was also important for the Sonogashira reaction: almost all reports and our experiment showed this feature. As general bases, Na_2CO_3, K_2CO_3, NaOH and KOH were tested and K_2CO_3 was found to be the best. K_2CO_3 was therefore selected as the base for our research. The reaction was carried out under a nitrogen atmosphere to avoid the oxidative coupling of terminal alkynes which generally takes place in the presence of oxygen.[14] Another notable advantage with this reaction was the recyclability of the PdCo catalyst. The catalyst could be reused after being separated from the solution and washed sufficiently with water and methanol. After being reused three times, the catalytic activity did not decrease significantly. Elemental analysis of the filtrate after the reaction demonstrated no leaching of Pd, implying that the reaction proceeded through a heterogeneous catalytic process.

Under optimized reaction conditions, the coupling of a series of aryl halides with terminal alkynes was studied. The results are shown in Table 1. Both aryl bromides and aryl iodides could react with aromatic or aliphatic terminal alkynes to give the corresponding coupling products with high yields. Furthermore, the reactions of aryl halides with electron-withdrawing or electron-donating groups did not show obvious differences. This means that the reaction is relatively insensitive to the electronic characteristics of the substituents. It is noteworthy that, compared to Hyeon's method,[7] the PdCo-catalyzed Sonogashira reaction described here gives a similarly high yield, but with marked differences: (i) the PdCo bimetallic hollow nanospheres can be easily obtained using our simple method and (ii) our reaction proceeds in water instead of the toxic organic solvent DIA. In addition, to determine the role of the cobalt in the PdCo hollow spheres in the catalytic process, Co hollow spheres prepared under similar conditions were used in the model reaction mentioned above. However the reaction was sluggish. It is currently not clear whether the catalytic activity of the PdCo bimetallic hollow spheres results from true bimetallic catalysis or only from the Pd nanostructure with its special morphology. More detailed work is in progress.

In summary, PdCo bimetallic hollow nanospheres of about 80 nm diameter and of about 9 nm thickness were synthesized in polyethylene glycol solution. To the best of our knowledge, this is the first example of Pd-containing bimetallic hollow nanospheres using soft template synthesis. Furthermore, they were successfully used to catalyze the Sonogashira reaction, which reveals obvious advantages such as environmentally friendly reaction conditions (the reaction proceeded in water), the recyclability of the catalyst, simple experimental operation and high yields. It is also a new application of palladium–cobalt nanoparticles in organic synthesis. Similar fabrication of Co, PdNi, Ag_2S, and CdS hollow spheres *via* polyethylene glycol-assisted route suggests that this simple, rapid and effective approach can be extended to prepare a variety of nanoscale hollow spheres. Further studies on organic synthesis of these metallic hollow nanospheres are under way in our laboratory.

Experimental

Analytical-grade cobaltous sulfate ($CoSO_4 \cdot 7H_2O$), palladium chloride ($PdCl_2$), sodium borohydride ($NaBH_4$), cuprous iodide (CuI), ammonium fluoride (NH_4F), and triphenylphosphine were purchased from Shanghai Chemical Reagents Co.

Table 1 The coupling of aryl halides with terminal alkynes using PdCo bimetallic hollow nanospheres as catalyst (see Scheme 1)

Entry	ArX	R	Time/h	Product	Yield[a](%)
1	PhI	Ph	6	**1a**[15]	92
2	*p*-$CH_3C_6H_4I$	Ph	6	**1b**[15]	87 (86, 87, 84)[b]
3	*m*-$CH_3C_6H_4I$	Ph	6	**1c**[15]	88
4	*o*-$CH_3C_6H_4I$	Ph	5	**1d**[16]	90
5	*p*-ClC_6H_4I	Ph	6	**1e**[18]	92
6	*p*-$O_2NC_6H_4I$	Ph	6	**1f**[15]	87
7	PhBr	Ph	8	**1a**	88
8	*p*-$CH_3C_6H_4Br$	Ph	8.5	**1b**	86
9	*p*-ClC_6H_4Br	Ph	8	**1e**	85
10	PhI	$CH_3(CH_2)_3$	6	**1g**[16]	88
11	*p*-$CH_3C_6H_4I$	$CH_3(CH_2)_3$	6	**1h**[16]	85
12	*m*-$CH_3C_6H_4I$	$CH_3(CH_2)_3$	6	**1i**[17]	92
13	*o*-$CH_3C_6H_4I$	$CH_3(CH_2)_3$	5.5	**1j**[16]	87
14	*p*-ClC_6H_4I	$CH_3(CH_2)_3$	6	**1k**[18]	93
15	PhBr	$CH_3(CH_2)_3$	8	**1g**	78

[a] Isolated yields. The products were characterized by ^1H NMR and IR spectra. [b] The catalyst was reused three times.

Polyethylene glycol (M_w 20 000) was purchased from Beijing Chemical Reagents Co. Phenylacetylene, *p*-iodotoluene, and other terminal alkynes and aryl halides were purchased from Aldrich. Organic solvents such as THF, acetonitrile, DMF, and isopropanol were distilled before use. H_2PdCl_4 solution was prepared by dissolving 500 mg $PdCl_2$ into 25 mL of hydrochloric acid (37%), then diluting with 50 mL of deionized water.

The PdCo bimetallic hollow nanospheres were fabricated as follows. To a solution of 2.5 g polyethylene glycol (M_w 20 000) in 10 mL of deionized water, 42 mg $CoSO_4 \cdot 7H_2O$, 25 mg NH_4F, 125 mg H_3BO_3 and 2.5 mL of H_2PdCl_4 solution were added in turn. Then the pH was adjusted to 7–8 using concentrated ammonia to form solution **A**. To 6 mL of 0.25 g mL^{-1} polyethylene glycol aqueous solution, 10 mg $NaBH_4$ were added to form solution **B**. Solution **A** was added slowly into solution **B** under sonication at 30–40 °C. The solution exhibited a colour change from colourless to black. After the addition of solution **A**, the resulting solution was further sonicated for 10 minutes. Finally, the black precipitate produced was separated from the mixture by centrifugation. The deposit was collected, washed with deionized water 4–5 times, and vacuum-dried. Thus the PdCo hollow nanospheres were obtained.

The synthesis of alkynes catalyzed by PdCo hollow nanospheres is as follows. To 3 mL of water were added 1 mmol of aryl halide and 1 mmol of terminal alkyne, then 0.05 mmol of palladium–cobalt nanoparticles, 0.2 mmol of PPh_3, 0.03 mmol of CuI and 1.5 mmol of K_2CO_3 were added in turn. The mixture was stirred at 80 °C under a nitrogen atmosphere for the appropriate time (see Table 1, monitored by TLC) till reaction was complete, then centrifuged. The solution was separated and the precipitate was washed with ether (5 mL × 3). The solutions were combined and extracted with ether and purified by column chromatography on silica gel with hexane–ethyl acetate (20 : 1) as eluent to yield the product (**1a–1k**, see Table 1). The precipitate was further washed sufficiently with water and methanol then dried, and the palladium–cobalt nanoparticles were recovered. After being reused three times, the yield of the product did not obviously decrease (a new batch of CuI and PPh_3 should be added when the catalyst was reused).

The characterization of the PdCo hollow nanospheres was performed by X-ray diffraction (XRD) using a D/Max-RA diffractometer with Cu Kα radiation, X-ray photoelectron spectroscopy (XPS) with Mg Kα ray source, energy dispersive spectroscopy (EDS), transmission electron microscopy (JEM-200CX TEM) and high-resolution transmission electron microscopy (JEOL 2010 HRTEM). For the structural determination of the Sonogashira reaction products, ^{1}H NMR spectra were determined on a Bruker spectrometer (300 MHz) with TMS as the internal standard. FTIR spectra were obtained with a Nexus 670 spectrometer. Melting points are uncorrected.

1a: Mp: 60 °C. ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.53–7.57 (m, 4 H), 7.35–7.41 (m, 6 H). IR (KBr) ν 3025, 1630, 1547 cm^{-1}.

1b: Mp: 71 °C. ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.53–7.56 (m, 2 H), 7.45 (d, J = 8.1 Hz, 2 H), 7.34–7.38 (m, 3 H), 7.18 (d, J = 7.8 Hz, 2H), 2.39 (s, 3 H). IR (KBr) ν 3018, 2235, 1630, 1547 cm^{-1}.

1c: Light yellow oil. ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.58–7.61 (m, 2 H), 7.37–7.43 (m, 5 H), 7.27–7.29 (m, 1H), 7.19 (d, J = 7.8 Hz, 1H), 2.40 (s, 3 H). IR (neat) ν 3015, 2228, 1645, 1556 cm^{-1}.

1d: Light yellow oil. ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.56–7.61 (m, 3 H), 7.38–7.42 (m, 3 H), 7.22–7.28 (m, 3 H), 2.57 (s, 3 H). IR (KBr) ν 3025, 2218, 1625, 1530 cm^{-1}.

1e: Mp: 81 °C. ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.47–7.57 (m, 4 H), 7.32–7.40 (m, 5H). IR (KBr) ν 3042, 2220, 1626, 1524 cm^{-1}.

1f: Mp: 118 °C. ^{1}H NMR δ (300 MHz, $CDCl_3$) 8.20 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 7.58–7.55 (m, 2H), 7.40–7.35 (m, 3H). IR (KBr) ν 3038, 2218, 1623, 1538 cm^{-1}.

1g: Light yellow oil. ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.40–7.42 (m, 2H), 7.28–7.32 (m, 3H), 2.41 (t, J = 6.9 Hz, 2H), 1.45–1.62 (m, 4H), 0.95 (t, J = 6.9 Hz, 3H). IR (neat) ν 3025, 2988, 2225, 1620, 1526 cm^{-1}.

1h: Light yellow oil. ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.26 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 2.39 (t, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.48–1.60 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H). IR (neat) ν 3022, 2945, 2210, 1625, 1528 cm^{-1}.

1i: Light yellow oil. ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.08–7.26 (m, 4H), 2.42 (t, J = 6.8 Hz, 2H), 2.33 (s, 3H), 1.48–1.63 (m, 4H), 0.95 (t, J = 6.8 Hz, 3H). IR (neat) ν 3038, 2958, 2216, 1620, 1534 cm^{-1}.

1j: Light yellow oil. ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.39 (d, J = 7.1 Hz, 1H), 7.12–7.20 (m, 3H), 2.48 (t, J = 7.0 Hz, 2H), 2.45 (s, 3H), 1.50–1.66 (m, 4H), 0.98 (t, J = 7.0 Hz, 3H). IR (neat) ν 3042, 2962, 2225, 1631, 1543 cm^{-1}.

1k: Light yellow oil. ^{1}H NMR δ (300 MHz, $CDCl_3$) 7.34 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 2.42 (t, J = 7.2 Hz, 2H), 1.45–1.63 (m, 4H), 0.97 (t, J = 7.2 Hz, 3H). IR (neat) ν 3045, 2968, 2234, 1630, 1554 cm^{-1}.

Acknowledgements

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