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Synthesis and Characterization of Novel Basketing of C-4-Phenylocta-phenylhydrazide-calix[4]resorcinarene-PdNPs

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Abstract. The novel synthesis basketing of C-4-phenylocta(phenylhydrazide)calix[4]resorcinarene-PdNPs/(K4ROPH-PdNPs). The route have been synthesized target compounds, including: (1) C-4-phenyloctahydroxycalix[4]resorcinarene (K4R), (2) C-4-phenyloctahydroxycalix[4]resorcinarene-acetate, (3) C-4-phenyloctaphenylhydrazidecalix[4]resorcinarene-amida (K4ROPH and (4) C-4-phenylocta(phenylhydrazide)calix[4]resorcinarene-PdNPs (K4ROPH-NPs). Compounds of K4ROPH-PdNPs were characterized carried out with FTIR, TEM, ^{1}H-NMR (500 MHz, DMSO-d6), and UV-Vis to determine ligands functional groups and particle size of ligands before and after being complexed with palladium transition metals. The results of particle size analysis using Transmission Electron Microscopy (TEM), obtained of K4ROPH-PdNPs have a particle size between 3-13 nm.

INTRODUCTION

Material of C-4-phenylocta(hydroxy)calix[4]resorcinarene material is macromolecular that it can be synthesized [1-7], and C-4-phenylocta(hydroxy)calix[4]resorcinarene materials in general can be used as an adsorbent only. This material to eliminate the presence of heavy metals methoxyphenylcalix[4]resorcinarene using to adsorb Pb(II), and Cr(III) [8], calix[4]resorcinarene tetraacetate using separation Pb(II) with Droplet Microreactor Systm [9], calix[4]arene derivative [10], poly-allyl-calix[4]arene-tetracarboxylic acid as adsorbent [11], poly-tetrapropenylcalix[4]arene as adsorbent [12,13], p-t.butylcalix[4]arene as adsorbent [14], poly-tetraallylcalix[4]arene-tetraacetic acid as adsorbent [15], calix[4]resorcinarene-chitosan hybrid as adsorbent [16]. Then some cali]4]arene and calix[4]resorcinarene were modified through etherification reaction by researchers calix[4]resorcinarene Sciff-bases [175], tetra-carboxymethylcalix[6]arene [18], mono(carboxy-methoxy)-tb-calix[4]arene [19], chitosan etherification [20], alkylation of ortho-methyl-tetra-C-naphtylresorcinarene [21]. Palladium catalyst has an important function, namely as a carbon-carbon coupling reaction. Derivative basketing Calix[4]pyrrole-palladium nanoparticles as reducing palladium(II) to palladium(0) using hydrazine materials [22,23]. This basketing nano palladium is in the form of a stable black solid inside the aqueous. Whereas in this research study the novelty value in the synthesis of the novel basketing C-4-phenylocta(phenylhydrazide)calix[4]resorcinarene as a reducing agent of palladium(II) to palladium(0) was used phenylhydrazine. Macromolecular material in which palladium metal is protected by C-4-phenylocta(penylhydrazide)calix[4]resorcinarene derivatives formed in novel basketing C-4-phenylcalix[4]resorcinarene derivatives as ligands with palladium(II) cations. The material of C-4-

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phenylocta(phenylhydrazide)calix[4]resorcinarene-PdNPs materials it can be synthesized through route reaction is the route I, condensation and cyclization reactions, route II, etherification reactions, route III, amidation reactions, and route IV, complexation reactions respectively. One method of synthesis of palladium nanoparticles is the reduction process of palladium(II) cations to palladium [0] neutral in the presence of phenylhydrazine groups. Some researchers related to the formation of etherification reactions [17-21], as well as continued route complexation between palladium (0) cations with derivatives C-4-phenylocta(phenylhydrzide)calix[4]resorcinarene [21-24]. The C-4-phenyl-octa(phenylhydrazide)calix[4]-resorcinarene-PdNPs material has been commonly applied to the mizoroki-heck carbon-carbon coupling reaction by researchers with trends surrounding in mechanistic discussion and investigation of the performance of palladium catalysts, cross-coupling reaction: mechanistic perspective [24], Nickel-catalyzed Mizoroki-Heck reaction [25], synthesis of monodisperse Palladium nanoparticle [26], Mizoroki-Heck reaction [27,28], Palladium(II)-catalyzed Heck reaction [29], Mechanistic study [30-33], Mizoroki-Heck reaction of aryl iodides [32], Palladium(II)-Schiff Base [35], Suzuki-Miyaura, Mizoroki-Heck carbon-carbon coupling [36], Mechanistic Investigation [37-40]. While this research will be synthesized C-4-phenylocta-(phenylhydrzide)calix[4]resorcinarene-PdNPs, and in a long time run it will be applied to the retrosynthetic process to synthesize leukemia cancer drug compounds using C-4-phenylocta(phenylhydrazide)calix[4]resorcinarene-PdNPs as a catalyst for Mizoroki-Heck reactions [22-23], and the purpose of synthesizing novel basketing C-4-phenylocta(phenylhydrazide)calix[4]resorcinarene-PdNPs to be applied as a carbon-carbon coupling catalyst in several medicinal plant compounds, such as sinamay derivatives, compared derivatives and have biological activity and potential as cancer leukemia drug compounds [41-43]. Synthesis Material of Lignin@PdNPs for too applied in Mizoroki-Heck Reaction [44]

EXPERIMENTAL

Materials

C-4-phenyllcalix[4]resorcinarene (K4R) according [1-5], C-4-phenyllcalix(ethoxy-carboxy)calix[4]resorcinarene (K4ROA) according to the procedures reported previously [17-21], C-4-phenyl(phenylhydrazide)calix[4]-resorcinarene (K4ROPH) according to the procedures reported previously [22-23], C-4-phenyl(phenylhydrazide)-calix[4]resorcinarene-nanopalladium (K4ROPH-PdNPs) were prepared from C-4-phenylcalix[4]resorcinarene according to the procedures reported previously [21,22][24]. The following chemicals, potassium carbonate (K_2CO_3), Resorcinol, Chloroform, phenylhydrazine, Ethyl-Bromoacetate, $PdCl_2$, Ethanol, HCl, Na_2SO_4 anhydroos. All material purchased were Merck

Instrumentation

The equipment used included infra-red (FT-IR, Shimadzu 8201 PC, KBr Pellet), Transmission Electron Microscopy (TEM) micrograph were recorded on a JEOL JEM – 1400 Electron. Microscope using an accelerated voltage of 120 kV, Spectrometry NMR JEOL (500 MHz, DMSO-d6), Spectrophotometry UV-Vis

Methods

Route I: Synthesis of C-phenylocta(hydroxyl)calix[4]resorcinarene (K4R) [1]

The results in the form of solids are characterized by FTIR at wave numbers (cm^{-1}); 3355,24; 1610,35 and 1452.

Route II: Synthesis of C-4-phenylocta(carboxy-methoxy)calix[4]resorcinarene (K4ROA) [17]

Weighed 0.639 grams of Calix[4]resorcinarene and added 2 grams of K_2CO_3 and dissolved in 50 mL chloroform and stirred for 30 minutes. Then 4 mL ethyl-bromoacetate was added to reflux for 72 hours of discontinue. Then the solids are filtered after all the filtrate is gone, then the solids are added to dilute HCl to remove the remaining sodium and at the same time hydrolyze the ester to carboxylic, then filtered and washed with ethanol yellow deposits will be obtained, then dried using a sitting lamp and the sediment will turn yellowish green (close to gray). Sediment was obtained as much as 0.330 grams. Then the FTIR were characterized.

Route III: Synthesis of C-4-phenylocta(phenylhydrazide)calix[4]resorcinarene (K4ROPH) [22]

Weighed 250 mg of C-4-phenyl-octa(carboxy-methoxy)calix[4]resorcinarene, dissolved in a mixture solution of methanol: chloroform is 25:25, the mixed mixture stirred until homogeneous for 30 minutes, then added 3 mL Phenylhydrazine dropwise and added reflux for 5 hours at 130^0 C. Then filtered and the precipitate washed with ethanol will get pale yellow deposits/solids. The filtered solids are washed with ethanol and dried (oven or heat from the lamp). The results obtained were 0.229 grams and then FTIR was characterized.

Route IV: Synthesis of C-4-phenylocta(phenylhydrazide)calix[4]resorcinarene-PdNPs [22, 23]

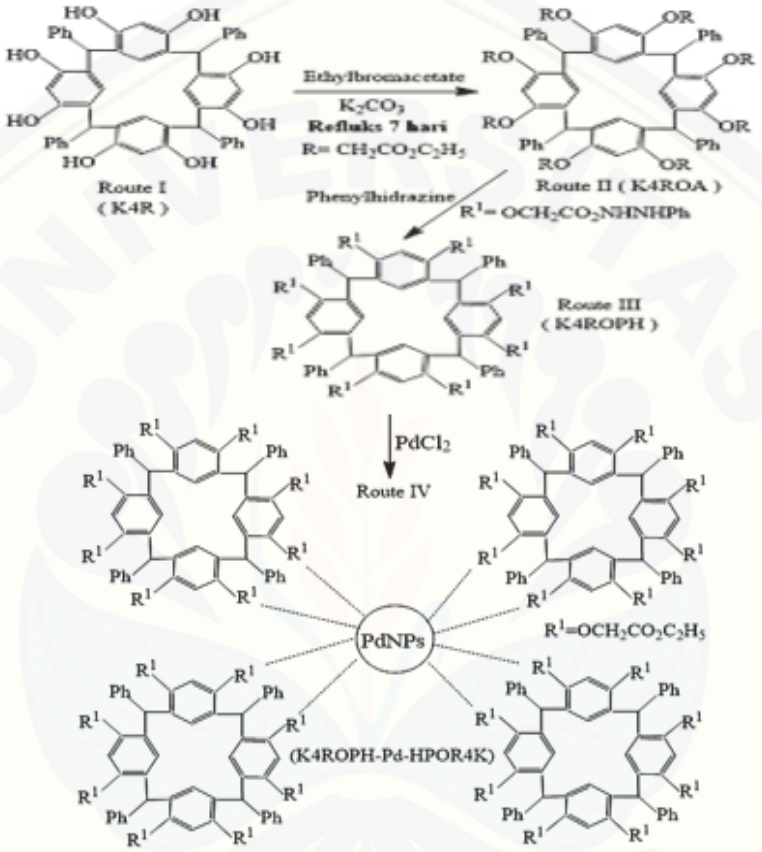

FIGURE 1. Synthesis of compounds: K4R, K4ROA, K4ROPH, and K4ROPH-PdNPs

Heated 100 mL of C-4-phenylocta(phenylhydrazide)calix[4]resorcinarene/K4ROPH (0.10 gr) ligand in water at a temperature of 50^0C and added $PdCl_2$ 0.01 grams dissolved in 100 mL ethanol while heated at 50^0C and stirring for 1 hour, then mixing while stirring for 1 hour After mixing the color changes from dark brown to blackish colloid. Then let stand for 2 hours blackish deposits will occur from K4ROPH-PdNPs and obtained as much as 115 mg of sediment weight. Then characterization using. The products obtained are grey-black solids from TEM and ^{1}H-NMR analysis. The size of C-4-phenylocta(phenylhydrazine)calix[4]resorcinarena-nanopalladium solids has nanoparticle size 3-13 nm.

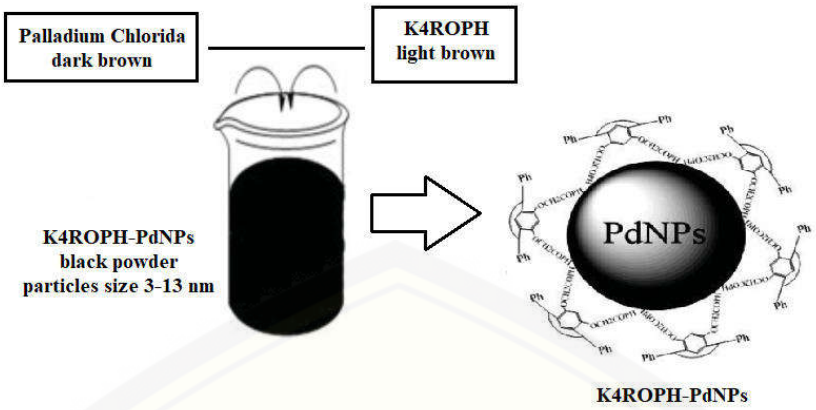

FIGURE 2. Schematic representation depicting the preparation of K4ROPH-PdNPs

RESULTS AND DISCUSSION

Characterization of K4R, K4ROA, K4ROPH, and K4ROPH-PdNPs using FTIR

Fourier transform infrared (FTIR) was employed to investigate the existence of stabilizing ligand of K4POPH on surface PdNPs. Fig. 3 Spectra FTIR the bands for (a) K4R (b) K4ROA (c) K4ROPH (d) K4ROPH-PdNPs, FTIR bands for Fig. 3(a), the bands at the interpretation with FTIR seen in the bands at 1612 cm^{-1} characterizes the presence of double bonds for aromatics and in the bands at 1427 cm^{-1}, which characterizes the presence of methylene groups (the presence of methylene bridges means cyclic-synthesized compounds) and in the bands at 3356.14 cm^{-1} characterizes of OH groups. Fig. 3(b), the bands at the interpretation of K4ROA with FTIR seen in the bands at 1612 cm^{-1} characterized the double bond for aromatics and the bands at 1720 cm^{-1} for C=O ester bending is characterizing the presence of characterizes an ester group. Fig. 3(c), the bands at the interpretation of K4ROPH (ligand) with FTIR seen in the bands at 1612 cm^{-1} characterized the double bond for aromatics and in the bands at 1427.32 cm^{-1} characterizing the presence of methylene groups (the presence of methylene bridges means cyclic-shaped compounds), investigated the presence of –CONHNPh amide the bonds bending from phenyl hydrazide because of there is a shift of wave numbers towards higher wavenumbers due to the conjugation system of the phenyl hydrazide groups the bands at 1951.96 cm^{-1} and –NH- groups the bands at 3402.43 cm^{-1}. Fig. 3 is FTIR spectra comparation of (a) K4R, (b) K4ROA, (c) K4ROPH, and FTIR spectra of 1(d) K4ROPH-PdNPs , the bands at of the interpretation of K4ROPH-PdNPs with FTIR seen in the bands at 1427.32 cm^{-1}, is characteristic of the presence of methylene groups, the bands at 1612.49 cm^{-1} characterize the existence of a double bond for aromatics, the bands at 1843,95 cm^{-1} is a complexing ligand (-NHN-Ph) with palladium metal and because of there is a shift of wave numbers towards higher wavenumbers due to the conjugation system of the phenyl hydrazide groups and –NH- groups the bands at 3402.43 cm^{-1}

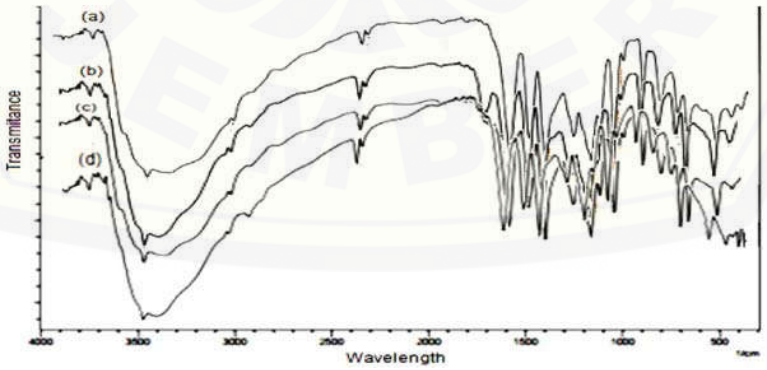

FIGURE 3. FTIR spectra of 3(a) K4R, 3(b) K4ROA, 3(c) K4ROPH, and 3(d) K4ROPH-PdNPs

Characterization of K4ROPH-PdNPs using TEM

Complexation reaction is K4ROPH-PdNPs with Palladium (II) Cations

Amphiphilic C-4-phenyloctacalix[4]resorcinarene-phenylhydrazide (K4ROPH) as both reducing and stabilizing agent to synthesize nanoparticles in particular, PdNPs. We have prepared PdNPs using palladium chloride and C-4-phenylocta-phenylhidrazide-calix[4]resorcinarene (K4ROPH) as a ligand in the water. In the water-dispersible K4ROPH-PdNPs were formed by one-pot route reducing is was a chemical reduction. The novel C-4-phenylocta-phenylhydrazide-calix[4]resorcinarene-PdNPs were investigated by FTIR, TEM, and UV-Vis. Based on the results of the analysis using FTIR on the following compounds it can be concluded that the synthesized compounds characterize the existing functional groups the characteristics of the synthesized compounds of K4ROPH-PdNPs at Fig. 4.

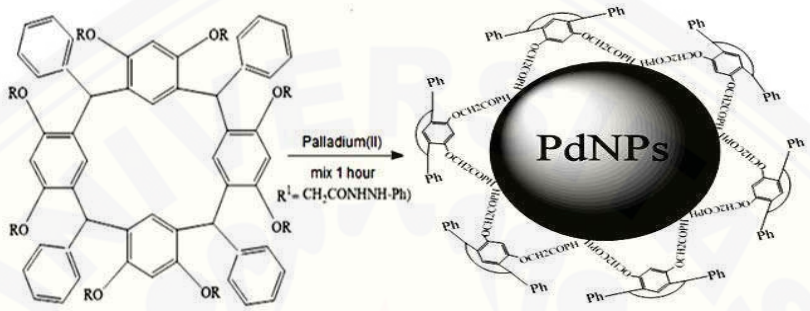

FIGURE 4. Complexation of ligand/ K4ROPH with Palladium(II) chloride

Investigation of K4ROPH-PdNPs using TEM

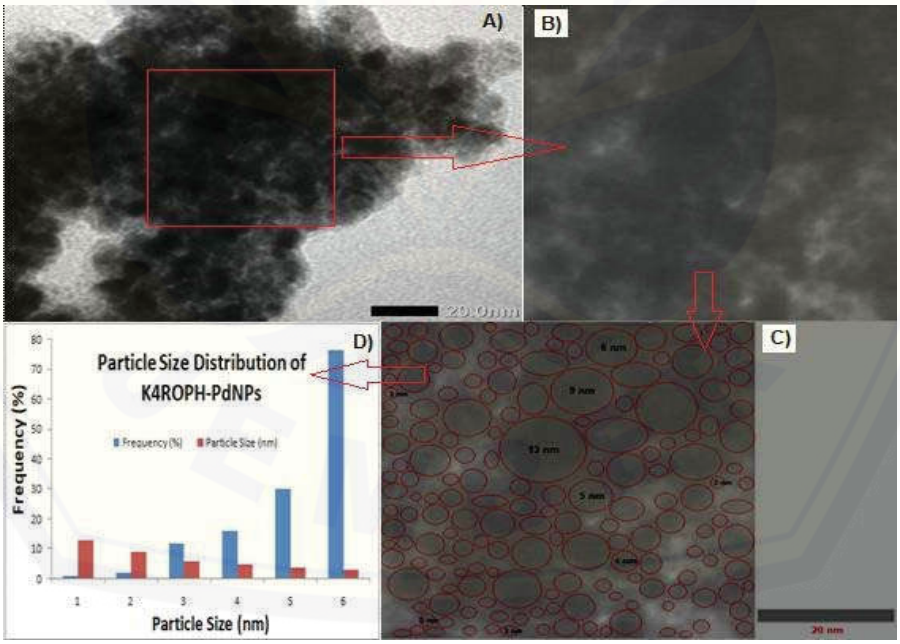

FIGURE 5. TEM micrographs: A). K4ROPH-PdNPs; B). Crop of K4ROPH-PdNPs; C). TEM image particle size (nm) of K4ROPH-PdNPs; D). Distribution particle size of K4ROPH-PdNPs.

From the results of the investigation of the Fig. 5 Morphology TEM image and after analysis of Fig. 5 obtained K4ROPH-PdNPs particle size, presented in Table 1 and yield of K4ROPH-PdNPs an investigation was carried out using ^{1}H-NMR of Fig. 6 follow.

TABLE 1 Particle size distribution of K4ROPH-PdNPs

No	Frequency (%)	Particle Size (nm)
1	1	13
2	2	9
3	12	6
4	16	5
5	30	4
6	70	3

Characterization of K4ROPH-PdNPs using ^{1}H-NMR

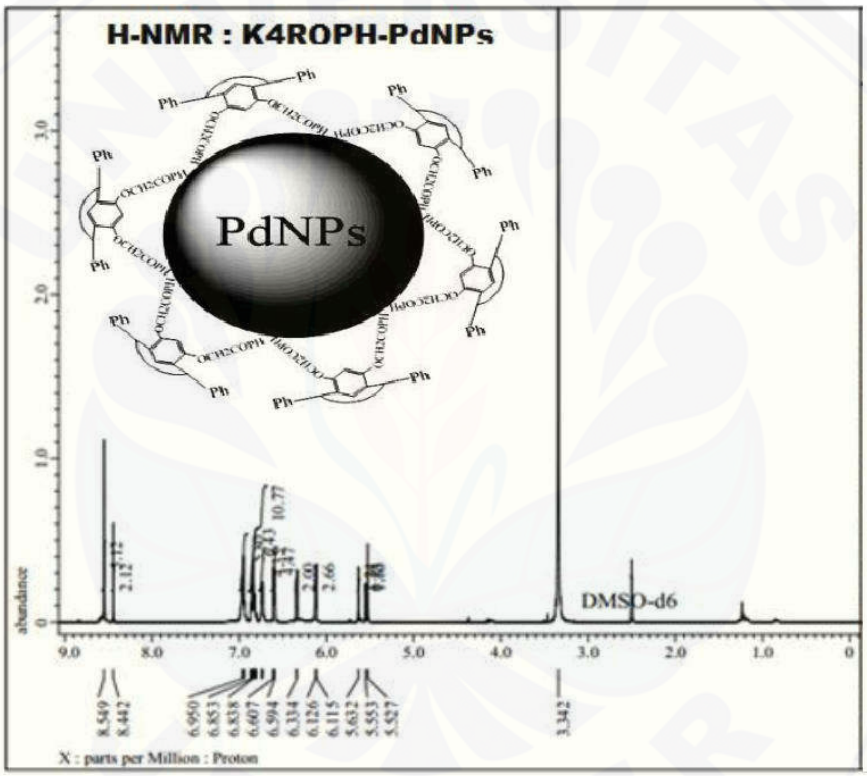

FIGURE 6 Spectrum ^{1}H-NMR (500 MHz, DMSO-d6) compound of K4ROPH-PdNPs

The product route (4) of compound C-4-phenylocta(phenylhydrazide)calix[4]resorcinarene-PdNPs Fig. 6 an investigation was carried out using ^{1}H-NMR spectroscopy (500 MHz, DMSO-d6), the appearance of chemical shift in the chemical shear in the region 5.527-5.553 ppm (4H,s,Ar-CH-Ar), 6,110-6,965 ppm (48H, broad d, ArH), 6.115-6.346 ppm (8H, d, OCH_2-CO), 8.442 ppm (4H,s,N-NH), and 3.433 ppm (solvent)

Characterization of K4ROPH-PdNPs and Palladium Chloride using UV-Vis

The profile of K4ROPH-PdNPs formed was characterized using UV-Vis spectroscopy. The addition of palladium chloride to K4ROPH solution using distilled water while heated showed a color change from light brown to black after 30 minutes which had previously stated the formation of colloidal K4ROPH-PdNPs at Fig. 7. The UV-Visible spectrum was taken to monitor and declare that K4ROPH-PdNPs had occurred. Palladium chloride solution gives broadband at λ 200-250 nm and band at λ_{max} 450 nm which refers to the presence of Pd (II) [21,22]. The loss of absorption bands at λ 200-250 nm and absorption bands at λ_{max} 450 nm from the analysis results were obtained

because of the reduction process of Pd(II) to Pd(0) at λ_{max} 450 nm is lost which states that the formation of K4ROPH-PdNPs at Fig. 7

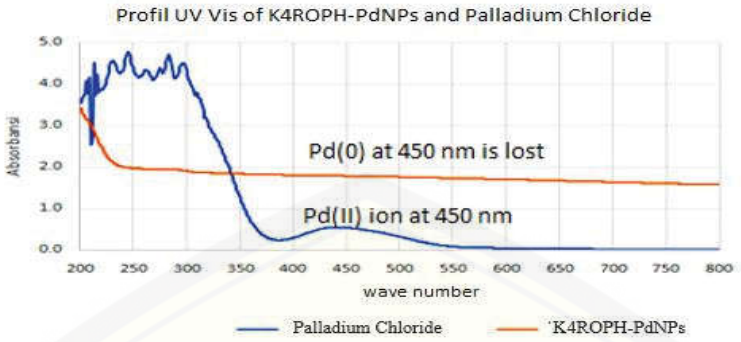

FIGURE 7. Spectra UV-Vis analysis of K4ROPH-PdNPs and solution of Palladium Chloride

CONCLUSION

The novel basketing material of C-4-Phenylocta(hydoxy)calix[4]resorcinarene or Calix[4]resorcinarene could be synthesized only in one pot of the reactions i.e. condensation of the resorcinol with benzaldehyde using HCl catalyst and simple direct only in one-pot chemical reduction method using an basketing C-4-phenylocta(phenylhydrazide)-calix[4]resorcinarene derivative for the preparation of small palladium nanoparticles. The targeting compounds was material novel basketing of C-4-phenylocta(phenylhydrazide)calix[4]resorcinarene-PdNPs and the results of particle size analysis using Transmission Electron Microscopy (TEM), it had particle sizes between 3-13 nm.

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