

Supporting Information

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A Polyphenylene Support for Pd Catalysts with Exceptional Catalytic Activity**

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1. Experimental methods.

Synthesis of Pd/PPhen composites. To obtain 2.7wt% Pd/PPhen, 1,2,4,5-tetrabromobenzene (0.765 g, 1.94 mmol) and benzene-1,4-diboronic acid (0.645 g, 3.89 mmol) were added into 60 mL dimethylformamide. The mixture was degassed through three freeze-pump-thaw cycles. K_2CO_3 (2.0 M, 7.5 mL) and $Pd(PPh_3)_4$ (0.225 g, 0.19 mmol) were then added with subsequent three freeze-pump-thaw cycles. The mixture was then purged with Ar and heated to 150 °C for 20 h under stirring. The product precipitated in water, and was washed by water, dichloromethane and methanol. Approximately 600 mg of grey product was obtained in each batch. The synthesis has also been carried out in air, similar structure is obtained. To synthesize Pd-free PPhen, the reaction temperature was reduced to 100 °C, maintaining the other reaction conditions. The amount of $Pd(PPh_3)_4$ was increased to 450 mg to obtain 5.9wt% Pd/PPhen. PVP ($M_w = 55,000$, 100 mg) was added into the synthesis to make the catalysts dispersible in water.

Synthesis of Pd/C, Pd/PDVB and Pd/TiO₂ catalysts. To obtain 2.7wt% Pd/C or Pd/PDVB, $Pd(PPh_3)_4$ (30 mg) was dissolved in 1 mL CH_2Cl_2 . The solution was added dropwise to Pd-free PPhen (100 mg), with subsequently calcination in 20% H_2/Ar at 250 °C for 3 h. 5wt% Pd/TiO₂ was prepared by impregnation of TiO₂ (Degussa P25) according to a reported method^[1].

$Pd(NO_3)_2 \cdot 2H_2O$ (25 mg) was dissolved in 2 mL H_2O . The solution was added dropwise into 200 mg TiO₂. The mixture was first dried at 80 °C for 16 h, with subsequent calcination in air at 400 °C for 3 h.

Suzuki coupling reactions. Typically, phenylboronic acid (91.5 mg, 0.75 mmol), sodium methoxide (81.0 mg, 1.5 mmol), 2.7wt% Pd/PPhen (15.7 mg, 4 μ mol) and PVP ($M_w = 55,000$, 0.5 mg) were added into 5 mL water. The solution was treated with ultrasound for 0.5 h, and 4-

chlorotoluene (63.3 mg, 0.50 mmol) and dodecane (35.0 mg, 0.21 mmol) were added. Dodecane acted as the internal standard. The mixture was degassed through three freeze-pump-thaw cycles, purged with Ar, and stirred at 80 °C for 3h. Toluene was added into the solution to extract the products. The products were analyzed by gas chromatography (GC) equipped with flame ionization detector (FID) for quantification. For other Suzuki coupling reactions, the same molar amounts of aryl chloride or arylboronic acid were added instead of 4-chlorotoluene or phenylboronic acid. For Suzuki coupling reactions with other catalysts, the same molar amount of palladium were added instead of Pd/PPhen. The molar ratio between palladium and substrates was kept constant. In the catalyst recycling experiments, after the reaction was concluded, the catalysts were separated by filtration, washed with ethanol, dried and weighed. In all cases, for the subsequent reaction cycle the weight ratio of substrates to catalyst was adjusted to the same value as in the first reaction.

Solvent-free benzyl selective alcohol oxidation in batch. Typically, benzyl alcohol (10.4g, 0.096 mol) and Pd/PPhen (10 mg, 2.5 μmol) or Pd/C was added into a glass inset inside a stainless steel autoclave reactor. The reactor was purged with O₂ and kept under 5 bar O₂. The reactor was then heated to 100 °C and stirred at 1500 rpm. The product was analyzed by GC-FID using dodecane as standard.

Benzyl alcohol selective oxidation in a gas-phase, plug-flow reactor. 2.7wt%Pd/PPhen (20 mg) or commercial 5wt%Pd/C (4 mg) or 5wt%Pd/TiO₂ (11 mg) was mixed with quartz sand (200 mg), and packed into a tubular reactor (6mm \times 160 mm). An evaporator for benzyl alcohol was connected to the inlet of the reactor. The temperatures of evaporator and reactor were controlled by individual ovens. Benzyl alcohol (0.1 mL·h⁻¹) was injected through a syringe pump into the evaporator and carried by O₂ (50 mL·min⁻¹) into the reactor. The partial pressure of benzyl

alcohol was controlled to be lower than its vapor pressure. The products were collected in a dry ice cooled-tetrahydrofuran solution with a gas outlet open to atmosphere. The solutions were periodically analyzed by GC-FID with dodecane as standard.

Characterization. HAADF-STEM imaging was carried out on an FEI Titan 80-300ST field-emission-gun (FEG) TEM operated at 300 kV. Electron tomography was performed by collecting tilt-series of HAADF-STEM images over a tilt range of -70° to $+75^\circ$ with a tilt increment of 2° . Alignment of the tilt series was performed using a collection of palladium nanocrystals (2-3.5 nm), indigenous to the Pd/PPhen composite, as fiducial markers. Tomogram reconstruction was carried out using a weighted back-projection algorithm in IMOD^[2]. Segmentation and 3D visualization of the different phases in the reconstructed volume was performed in Avizo (FEI). SEM imaging was performed on a Hitachi S-5500 FEG SEM. XRD measurement was performed on a Stoe STADI P Bragg-Brentano diffractometer with Cu $K\alpha_{1,2}$ radiation, using a secondary graphite monochromator. Solid densities were determined in a Micromeritics Accupyc 1330 gas pycnometer. N_2 adsorption isotherms were measured on Micromeritics ASAP 2010 adsorption analyzer at 77 K after activation in vacuum at 250°C for 24 h. XPS analyses were performed on a Kratos HSi spectrometer with a hemispherical analyzer. The monochromatized Al $K\alpha$ X-ray source ($E=1486.6\text{ eV}$) was operated at 15 kV and 15 mA. An analyzer pass energy of 40 eV was applied for the narrow scans. The hybrid mode was used as lens mode. The base pressure during the experiment in the analysis chamber was $45\times 10^{-7}\text{ Pa}$. All spectra were charge corrected referred to the C1s photopeak at 284.5 eV. TG measurements were performed on a Netzsch STA 449C thermal analyzer with a heating rate of $10^\circ\text{C min}^{-1}$. The solid-state NMR spectra were recorded on a Bruker Avance 500WB spectrometer using a double-bearing standard MAS probe (DVT BL4) at resonance frequencies of 125.8 MHz and 202.5 MHz for ^{13}C and ^{31}P ,

respectively. High-power proton decoupling (CW) and spinning rates between 10 and 12 kHz were applied for all spectra.

2. Supporting Figures.

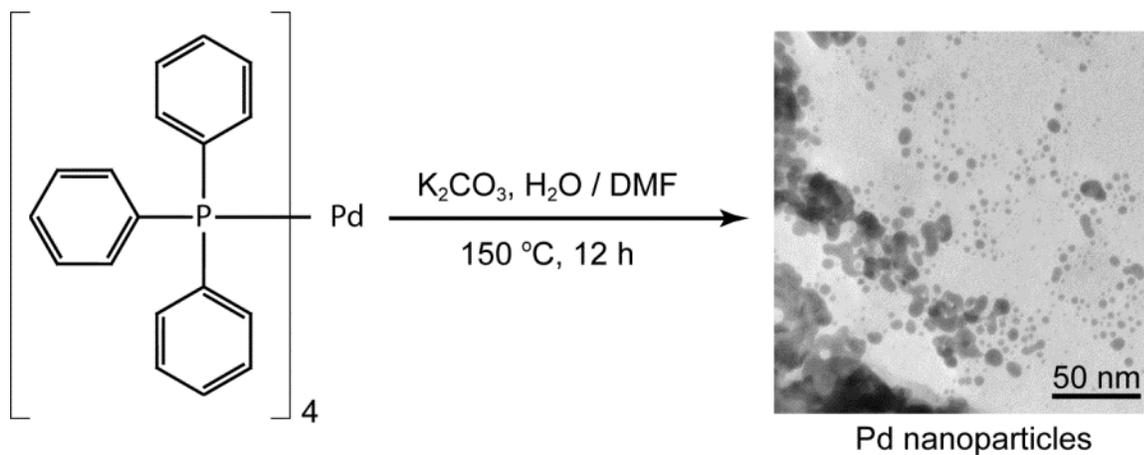


Figure S1. Reaction conditions of palladium precipitation by decomposition of $\text{Pd}(\text{PPh}_3)_4$ and representative bright-field TEM micrograph of the resulting palladium nanoparticles. The decomposition of $\text{Pd}(\text{PPh}_3)_4$ in DMF occurs at temperature above $110\text{ }^\circ\text{C}$.

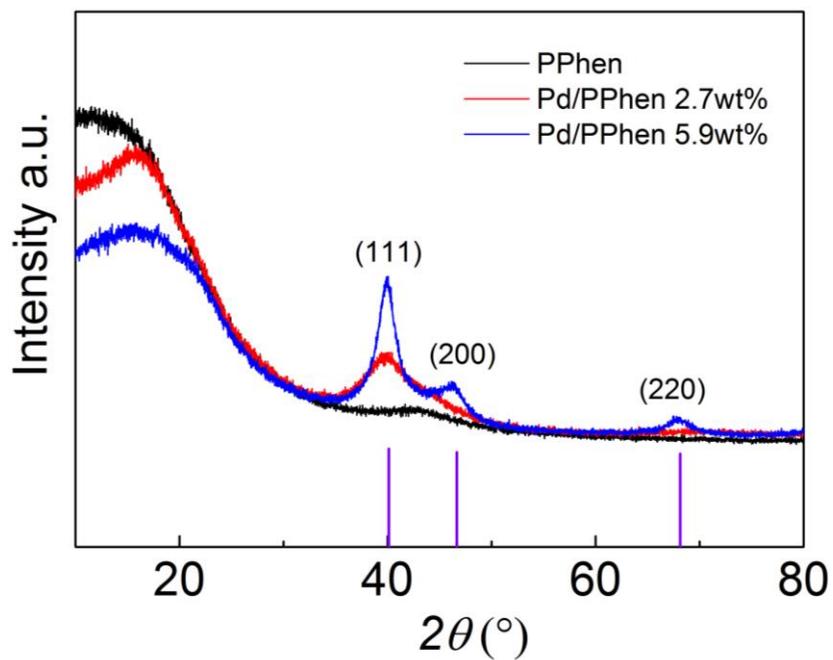


Figure S2. X-ray diffraction patterns of Pd/PPhen composites with different Pd loading (see legend) as well as the Pd-free PPhen support material obtained via sequential leaching treatments of the 2.7 wt% Pd/PPhen composite in aqueous H₂O₂ and HCl solutions. The indicated reflections correspond to metallic palladium.

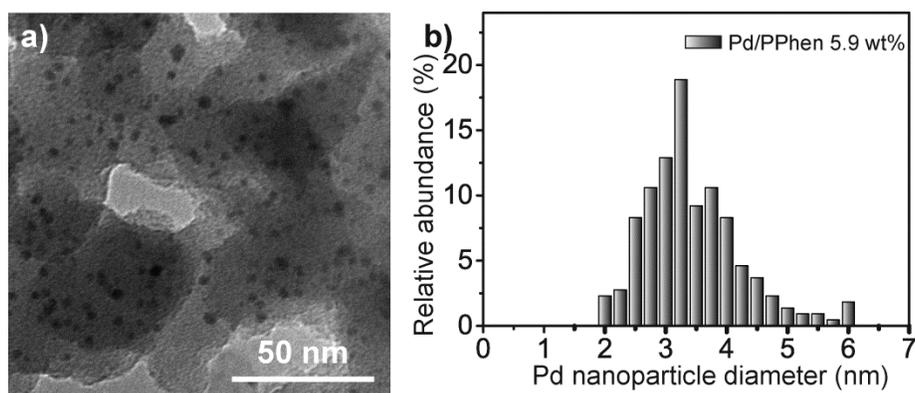


Figure S3. a) TEM image of 5.9 wt% Pd/PPhen. To obtain 5.9 wt% Pd/PPhen, the molar ratio of Pd(PPh₃)₄ to C-C coupling substrates was twice the normal ratio. b) Size distribution.

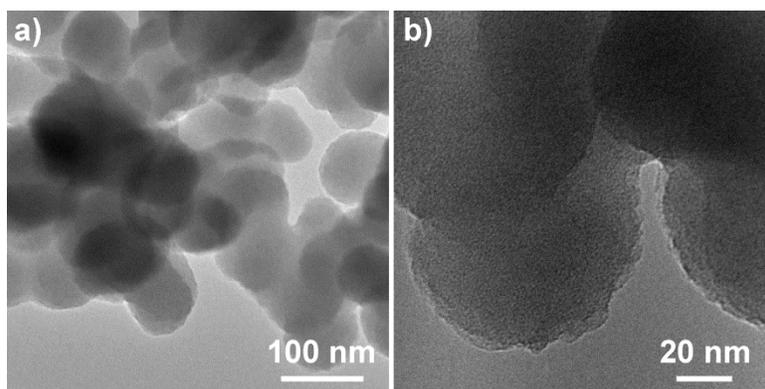


Figure S4. Bright-field TEM micrographs of the metal-free polyphenylene polymer obtained by Suzuki C-C coupling reaction of 1,2,4,5-tetrabromobenzene and benzene-1,4-diboronic acid at 100 °C. Pd(PPh₃)₄ in DMF does not decompose at this temperature, resulting in the Pd-free PPhen. a) TEM image at low magnification. b) TEM image at high magnification.

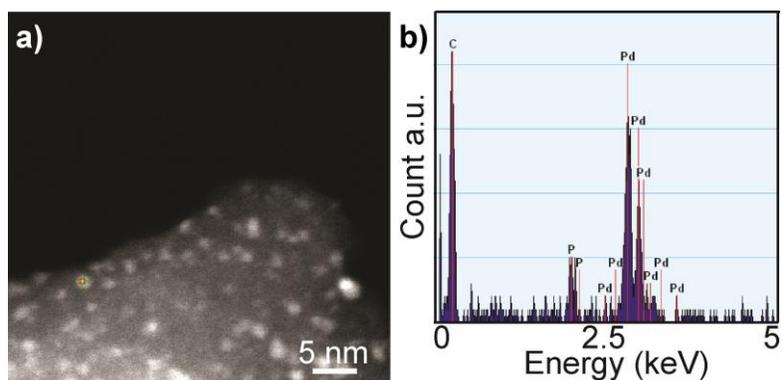


Figure S5. a) HAADF-STEM image of Pd/PPhen. b) Single dot EDX spectrum of the particle indicated as green cross in a).

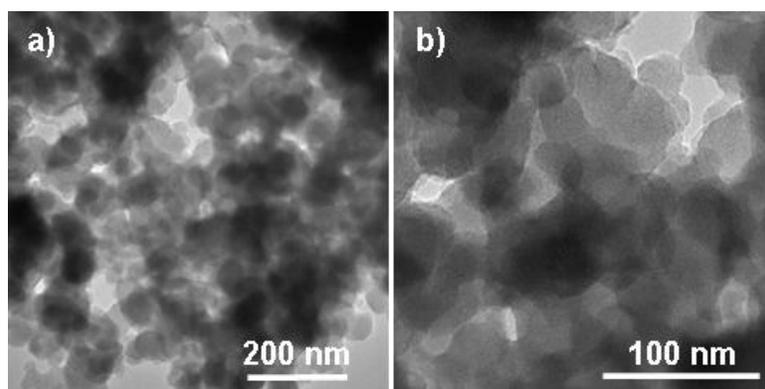


Figure S6. Bright-field TEM micrographs of the Pd-free polyphenylene polymer after palladium leaching by HCl and H₂O₂ treatments. H₂O₂ oxidizes palladium in to PdCl₂, resulting in the Pd-free PPhen. a) TEM image at low magnification. b) TEM image at high magnification.

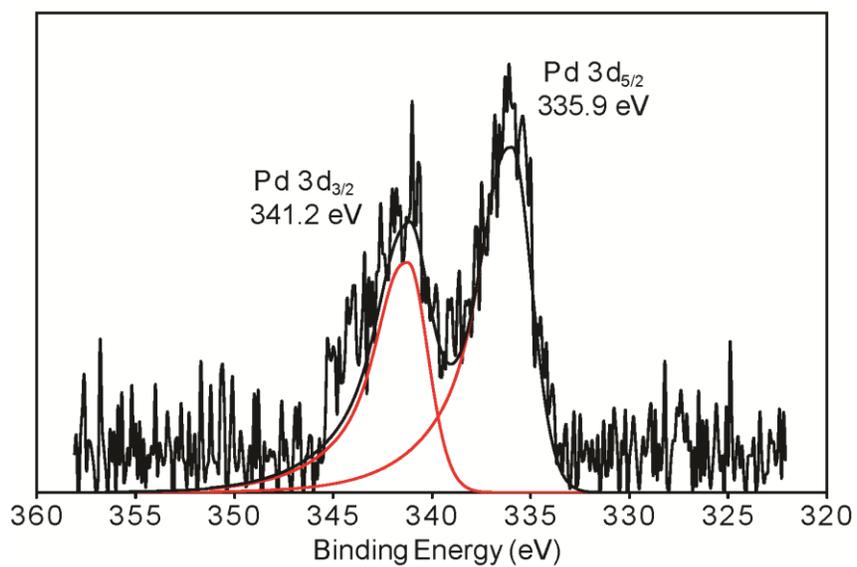


Figure S7. X-ray photoemission spectrum of 2.7wt%Pd/PPhen composite showing the characteristic 3d signals of metallic palladium. No indication of Pd (II) was found for these materials.

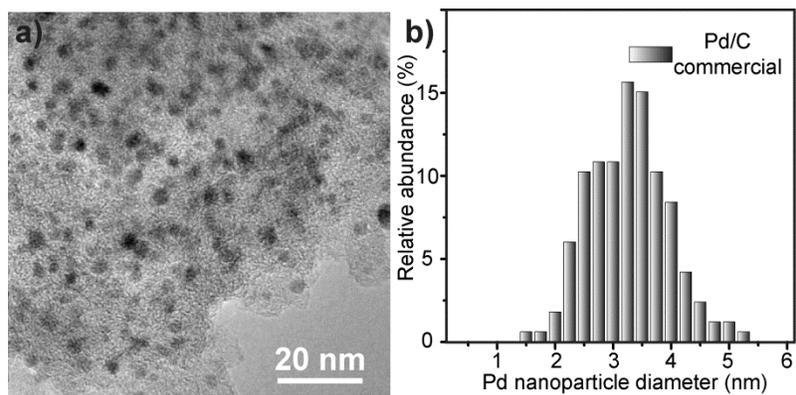


Figure S8. Bright-field TEM micrograph a) and corresponding palladium particle size histogram b) of a commercial Pd/C catalyst (Sigma-Aldrich). The size of palladium particles is in the range of 1.5-5 nm.

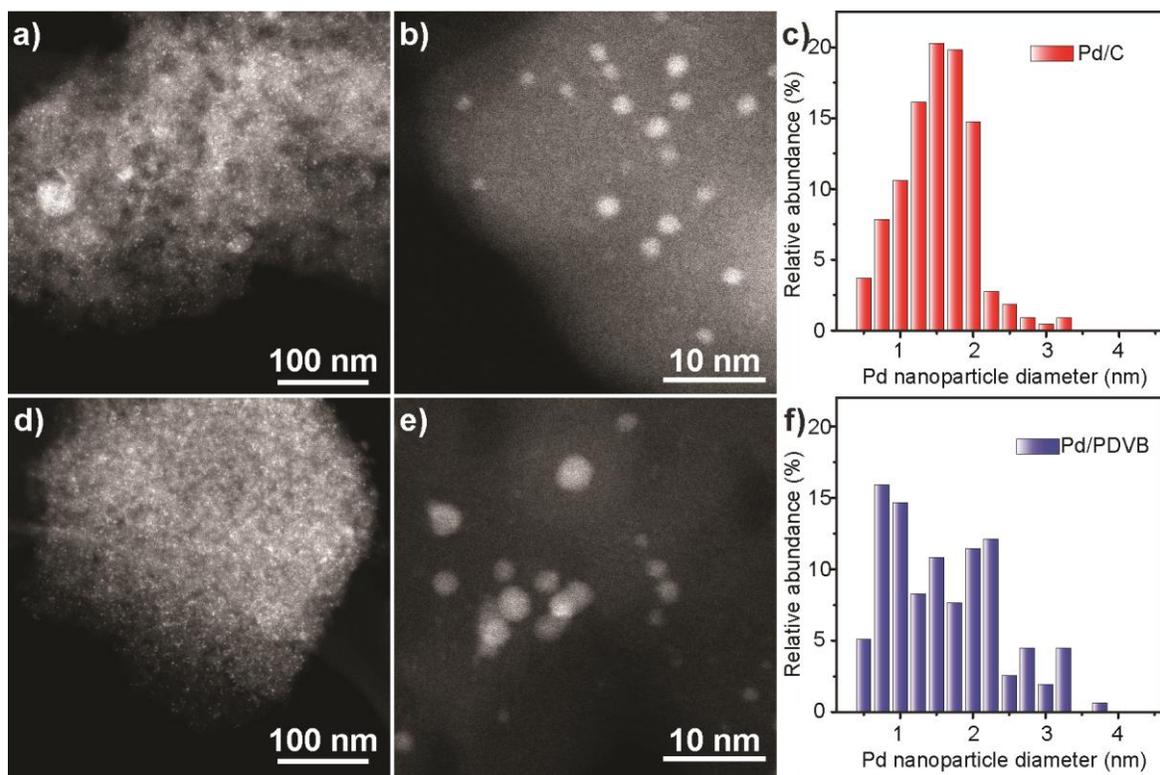


Figure S9. HAADF-STEM micrographs of a,b) 2.7wt% Pd/C and d,e) 2.7wt% Pd/PDVB catalysts prepared via impregnation of Pd(PPh₃)₄ on the supports followed by thermal decomposition/reduction in flow of 20% H₂/Ar. Palladium particle size distribution of c) 2.7wt% Pd/C and f) 2.7wt% Pd/PDVB.

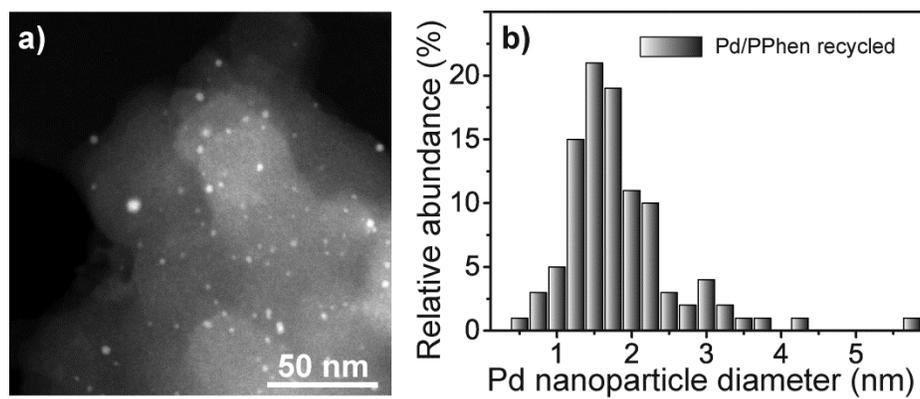


Figure S10. a) HAADF-STEM image of 2.7wt% Pd/PPhen catalyst after 4 consecutive recycles in the Suzuki coupling reaction of 4-chlorotoluene and phenylboronic acid. b) size distribution.

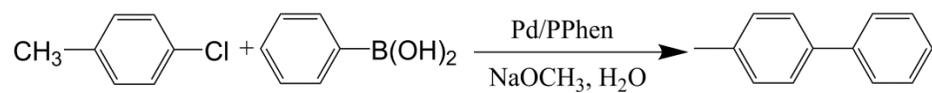
3. Supporting Tables.

Table S1. Wetting and dispersion of Pd/PPhen in different solvents.

Solvent	Dispersion
Benzene	Yes
Toluene	Yes
CH ₂ Cl ₂	Yes
CH ₃ OH	Yes
C ₂ H ₅ OH	Yes
Benzene alcohol	Yes
acetone	Yes
THF	Yes
Diglyme	Yes
DMF	Yes
H ₂ O	No
H ₂ O (PVP) ¹	Yes

¹10wt% of PVP is added in order to disperse Pd/PPhen in water.

Table S2. Recycling of the Pd/PPhen catalyst for Suzuki coupling reaction.



Reaction cycle	Product yield (%)
Initial run	82
1	79
2	82
3	84
4	78

4. Supporting Movie.

Movie S1. Representative aligned HAADF HR-STEM tilt series.

The video shows a representative aligned HAADF HR-STEM tilt series. Palladium nanoclusters and nanocrystals in the size range of 0.5-4 nm are observed. They are evenly distributed throughout the polymer host.

Video	Composites	File type/size
Movie S1	2.7wt% Pd/PPhen	QuickTime/17 MB

5. Supporting Reference.

- [1] J. K. Edwards, B. E. Solsona, P. Landon, A. F. Carley, A. Herzing, C. J. Kiely, G. J. Hutchings, *J. Catal.* **2005**, 236, 69-79.
- [2] J. R. Kremer, D. N. Mastronard, J. R. McIntosh, *J. Struct. Biol.* **1996**, 116, 71-76.