Supplementary Material (ESI) for Green Chemistry
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Supplementary Information

Synthesis of Pd Nanocrystals in Phosphonium Ionic Liquids Without External Reducing Agents

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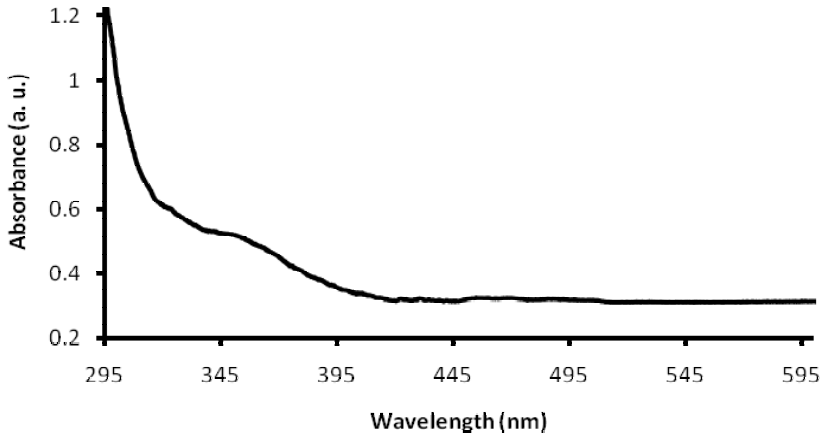

Figure S1. UV-vis spectrum of Pd nanocrystals prepared from reduction of $Pd(CH_3CN)_2Cl_2$ in $[P_{66614}]DBS$. 60 mg of the reaction mixture was diluted in 5 mL of dichloromethane.

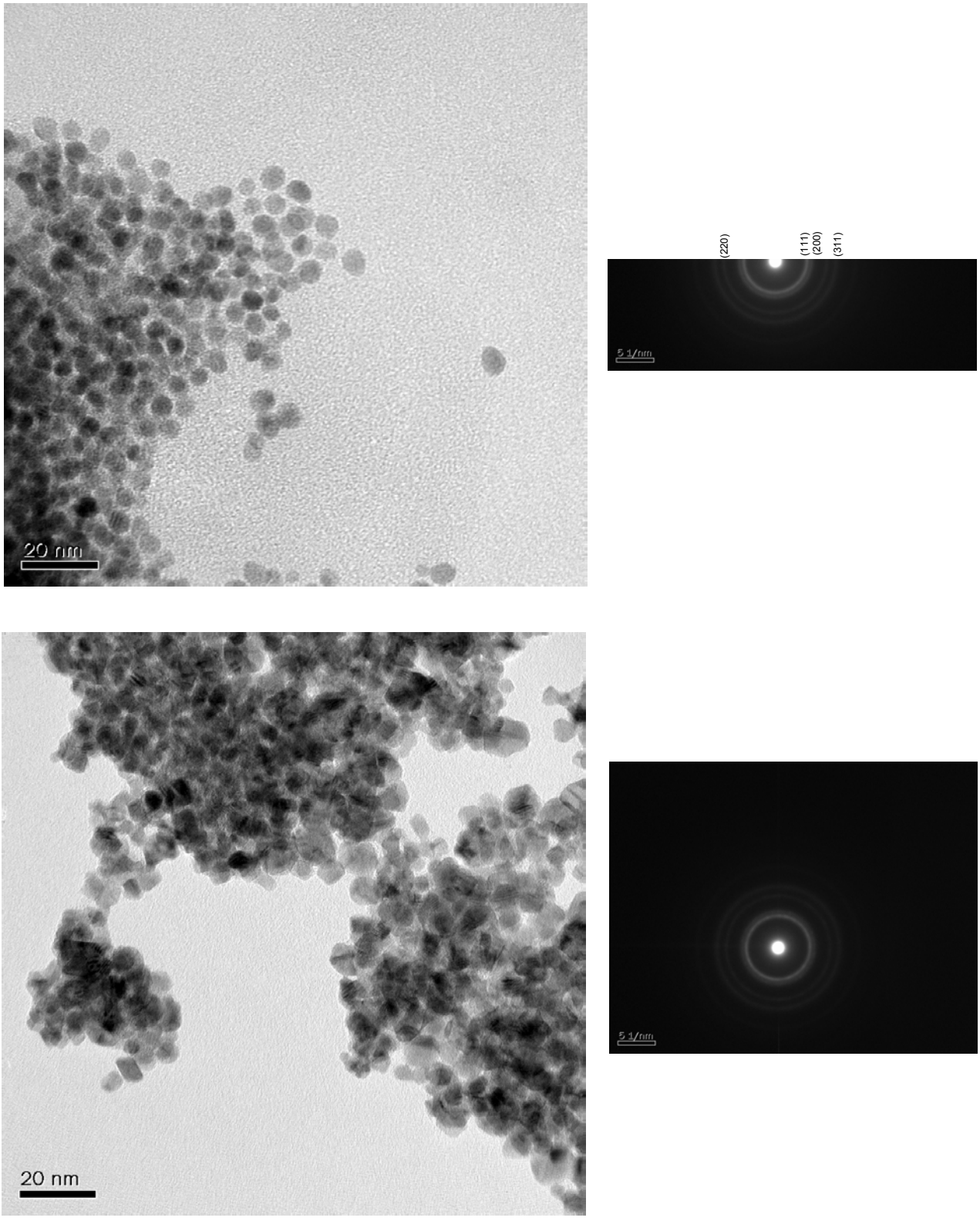

Figure S2. TEM image of the Pd nanocrystals (and the corresponding selected area electron diffraction patterns) synthesized from dissolved $Pd(CH_3CN)_2Cl_2$ (top) and $Pd(OAc)_2$ (bottom) in $[P_{66614}]DBS$.

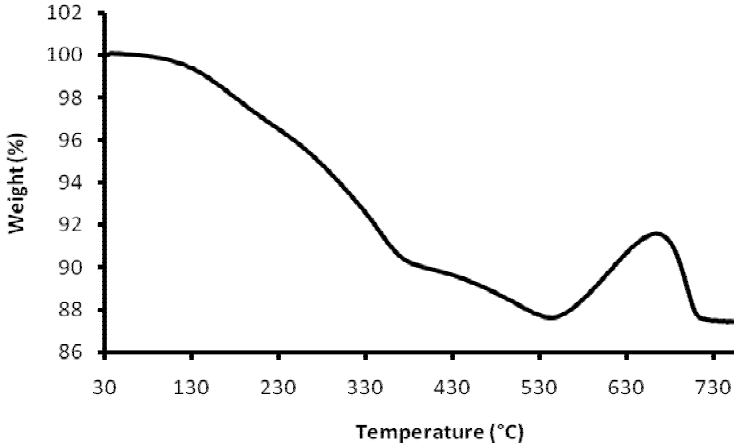

Figure S3. Thermogram of Pd nanocrystals. Sample was heated with a ramp of 20 °C/min under nitrogen flow. Approximately 10 wt% loss is seen between 30 °C and 350 °C.

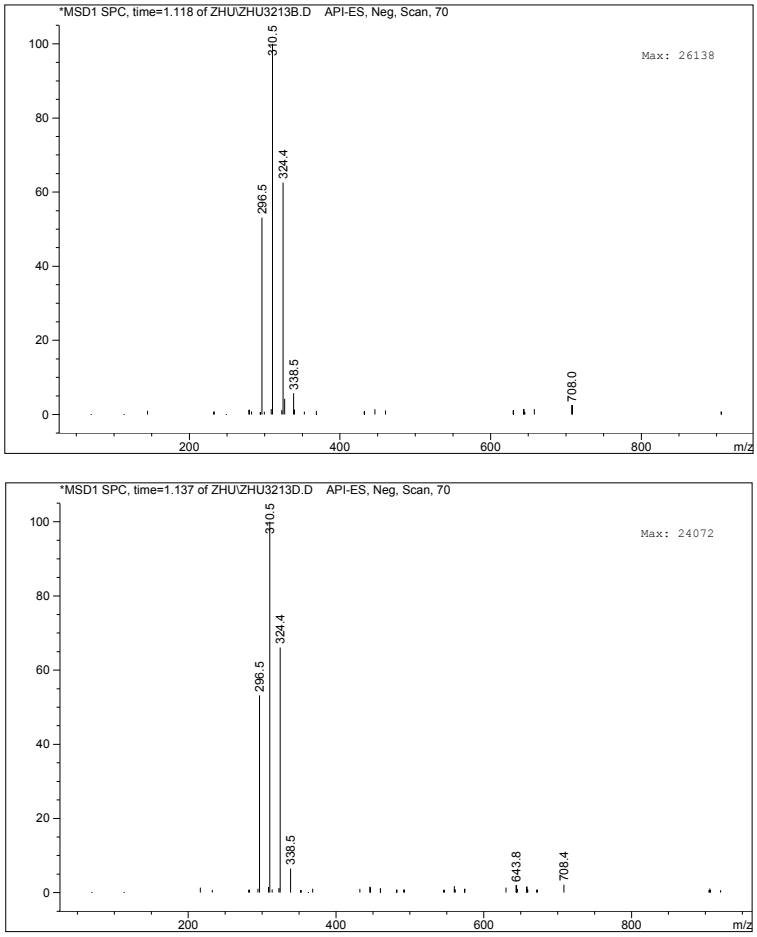

Figure S4. ESI-MS spectrum (negative scan) of $[P_{66614}]$DBS before (top) and after (bottom) the synthesis of Pd nanocrystals.

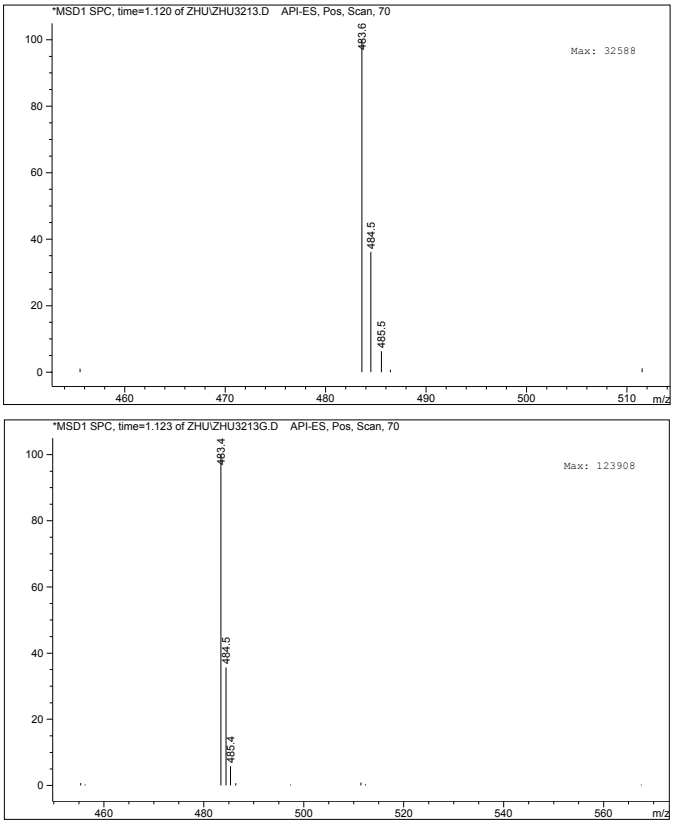

Figure S5. ESI-MS spectrum (positive scan) of $[P_{66614}]$DBS before (top) and after (bottom) the synthesis of Pd nanocrystals.

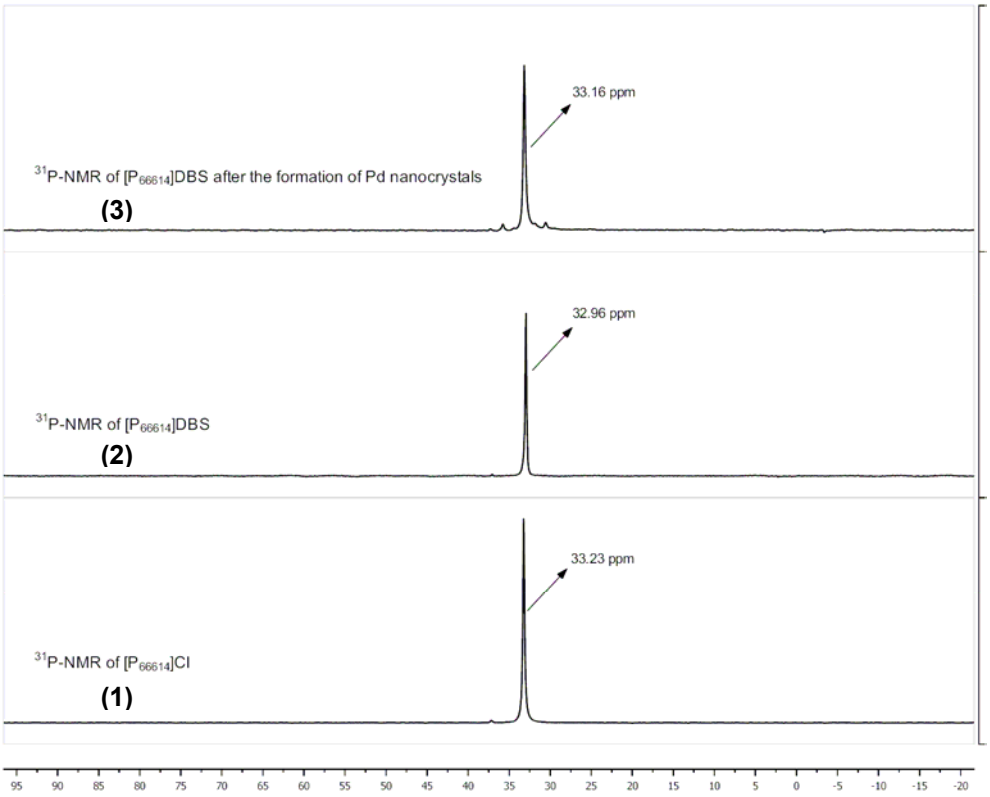

Figure S6. ^{31}P-NMR of neat $[P_{66614}]$Cl (spectrum 1, $\omega_{1/2}$ = 60 Hz), neat $[P_{66614}]$DBS (spectrum 2, $\omega_{1/2}$ = 48 Hz) and $[P_{66614}]$DBS after the formation of Pd nanocrystals (spectrum 3, $\omega_{1/2}$ = 74 Hz).

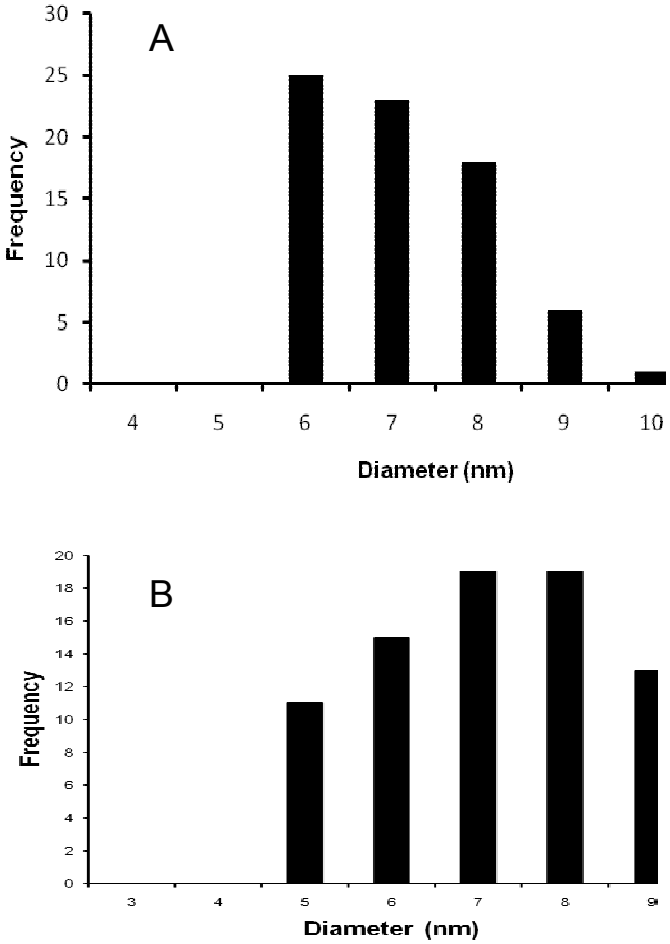

Figure S7. Size distribution histograms of Pd nanocrystals synthesized from the reaction of $Pd(CH_3CN)_2Cl_2$ in $[P_{66614}]$DBS (A) and $Pd(CH_3CN)_2Cl_2$ in $[P_{66614}]$bis(trifluoromethylsulfonyl)amide (B).

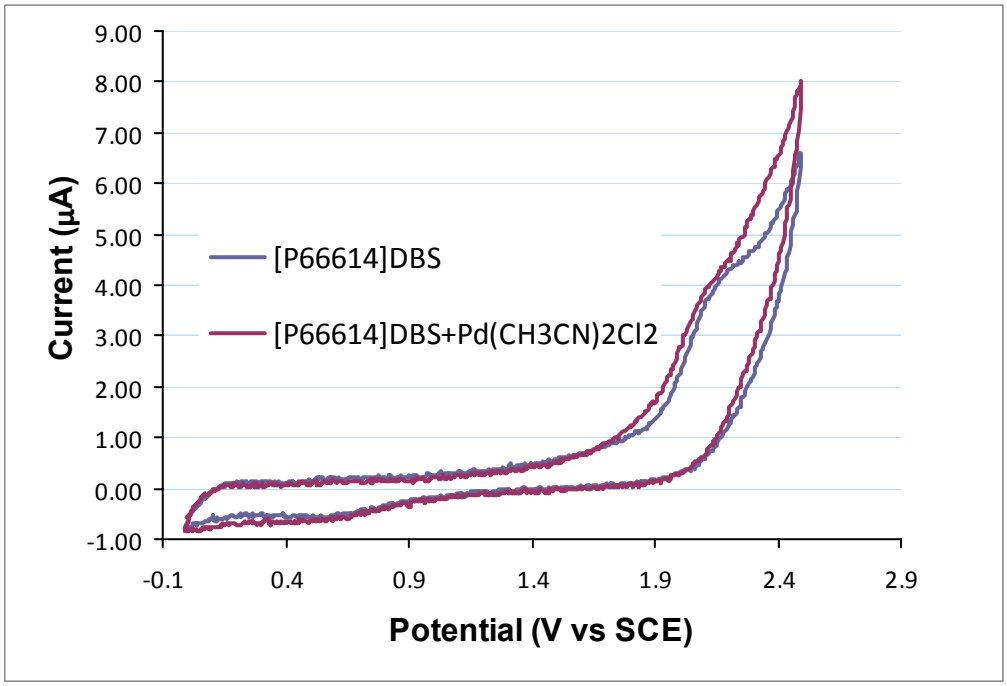

Figure S8. Cyclic voltammagrams in CH_3CN for **1** (4.0 mmol L^{-1}) in blue, and **1** (4.0 mmol L^{-1}) with $Pd(CH_3CN)_2Cl_2$ (1.3 mmol L^{-1}) in red. Working electrode = Pt disk (0.0045 cm^2), counter electrode = high surface area Pt wire and reference electrode = saturated calomel electrode (SCE). Scan rate, in both experiments, was 200 mV s^{-1}. The value vs. Fc/Fc^+ in CH_3CN can be calculated from the values vs. SCE by subtracting 0.47 V.

Note: Viscosity is an important factor in electrochemistry due to the necessary migration of species in solution. Phosphonium ILs with long alkyl chains (such as **1**) are not recommended for electrochemical purposes without a co-solvent as they are more viscous than their short-chain counterparts.

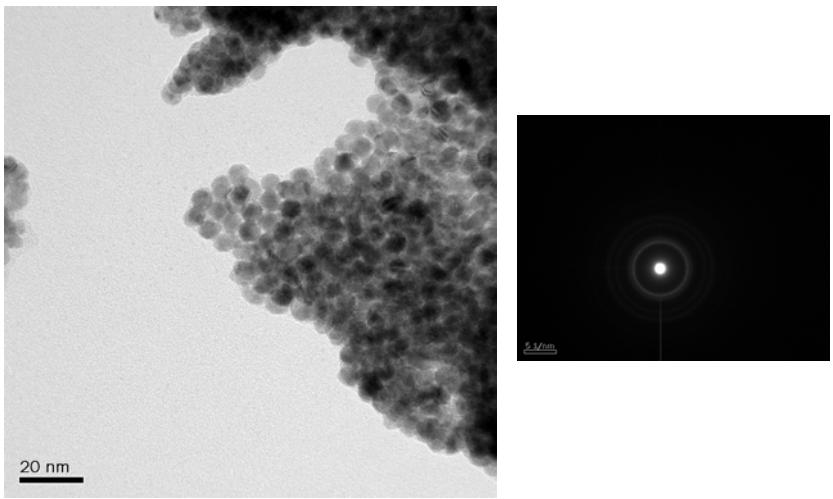

Figure S9. TEM image of the Pd nanocrystals (and the corresponding selected area electron diffraction pattern) synthesized from dissolved $PdCl_2$ in $[P_{66614}]DBS$

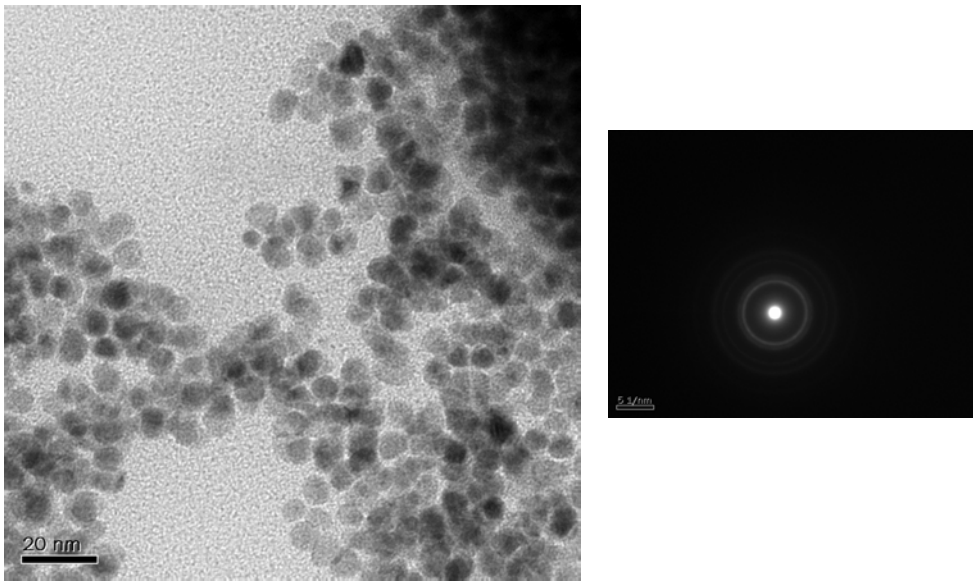

Figure S10. TEM image of the Pd nanocrystals (and the corresponding selected area electron diffraction patterns) synthesized from dissolved $Pd(CH_3CN)_2Cl_2$ in $[P_{66614}]$bis(trifluoromethylsulfonyl)amide.

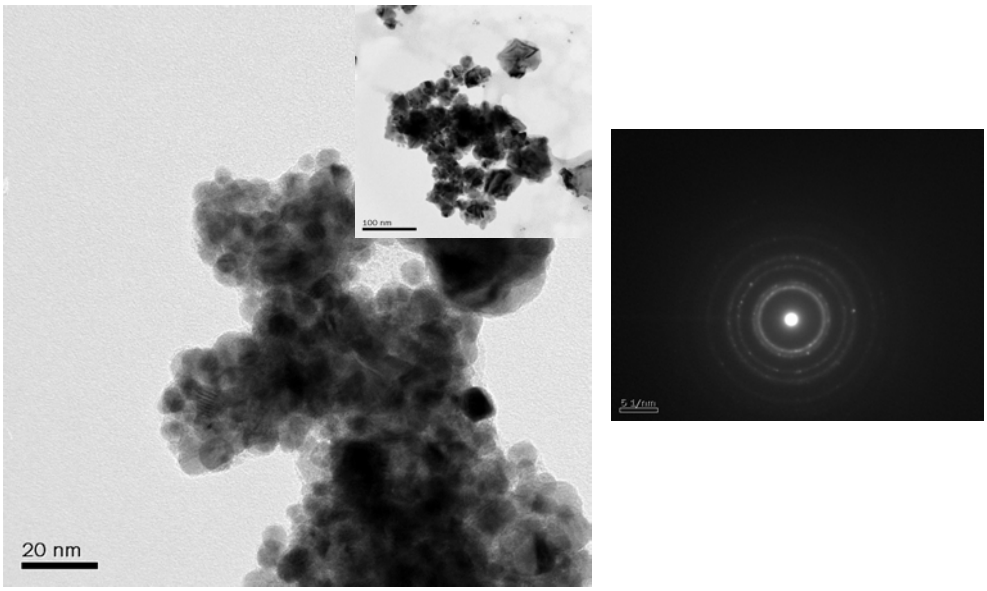

Figure S11. TEM image of the Pd nanocrystals (and the corresponding selected area electron diffraction patterns) synthesized from dissolved $Pd(CH_3CN)_2Cl_2$ in $[P_{66614}]$hexafluorophosphate.

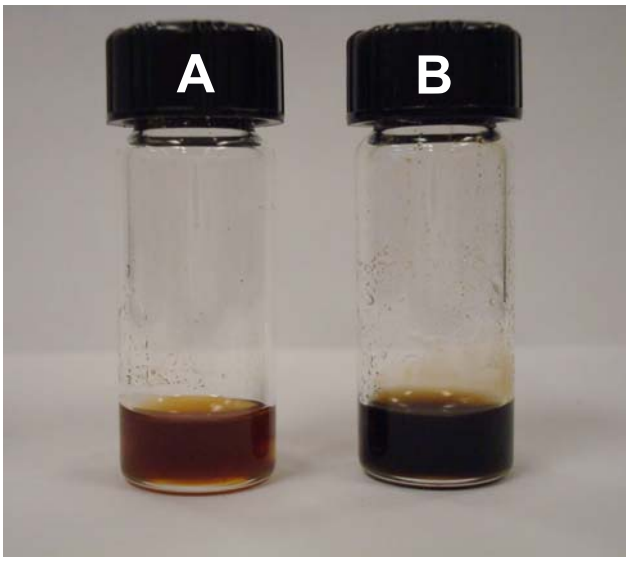

Figure S12. Oxidative etching effect on the reaction. In this study, the same amount of $Pd(CH_3CN)_2Cl_2$ was dissolved in dried and degassed $[P_{66614}]DBS$. The solutions were stirred with the same speed on the benchtop (A) and in glove box (B) for 18 h.

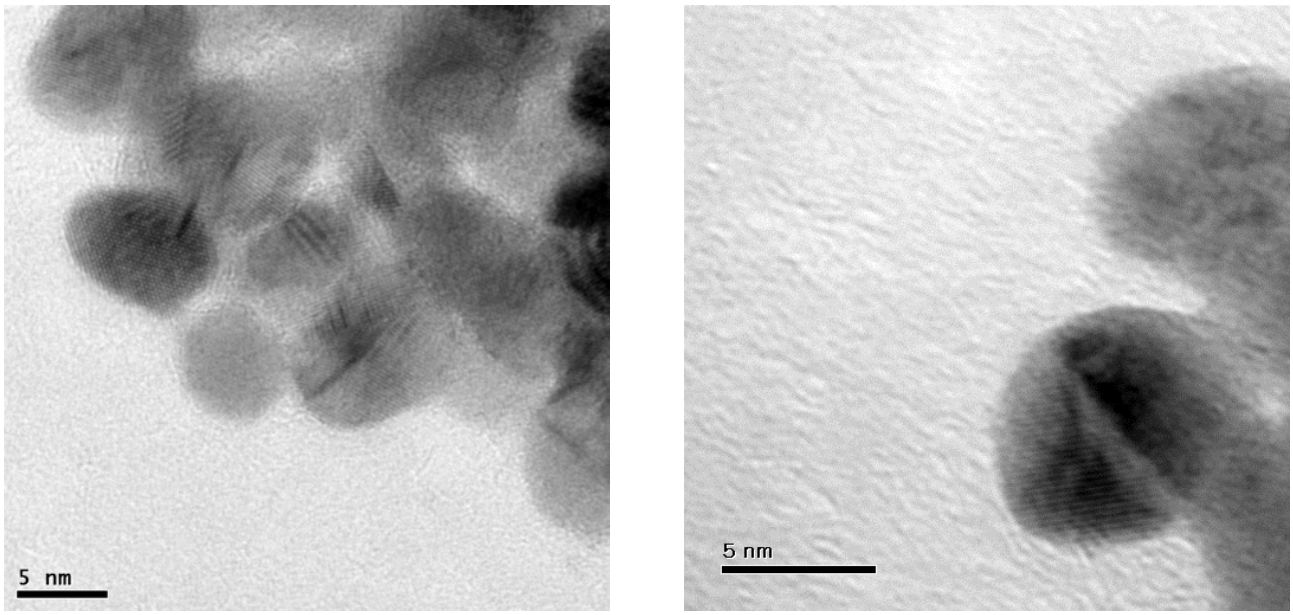

Figure S13. HRTEM images of the Pd nanocrystals prepared from $Pd(CH_3CN)_2Cl_2$ in a 1:1 mole ratio mixture of $[P_{66614}]DBS$ and THF at room temperature. Stacking defects are observable in the images.