

# Simple procedure for vacant POMs-stabilized palladium (0) nanoparticles in water: structural and dispersive effects of lacunary polyoxometalates

R. Villanneau,<sup>\*a,b</sup> A. Roucoux,<sup>\*c</sup> P. Beaunier,<sup>d,e</sup> D. Brouri,<sup>d,e</sup> and A. Proust<sup>a,b</sup>

## Supplementary Informations

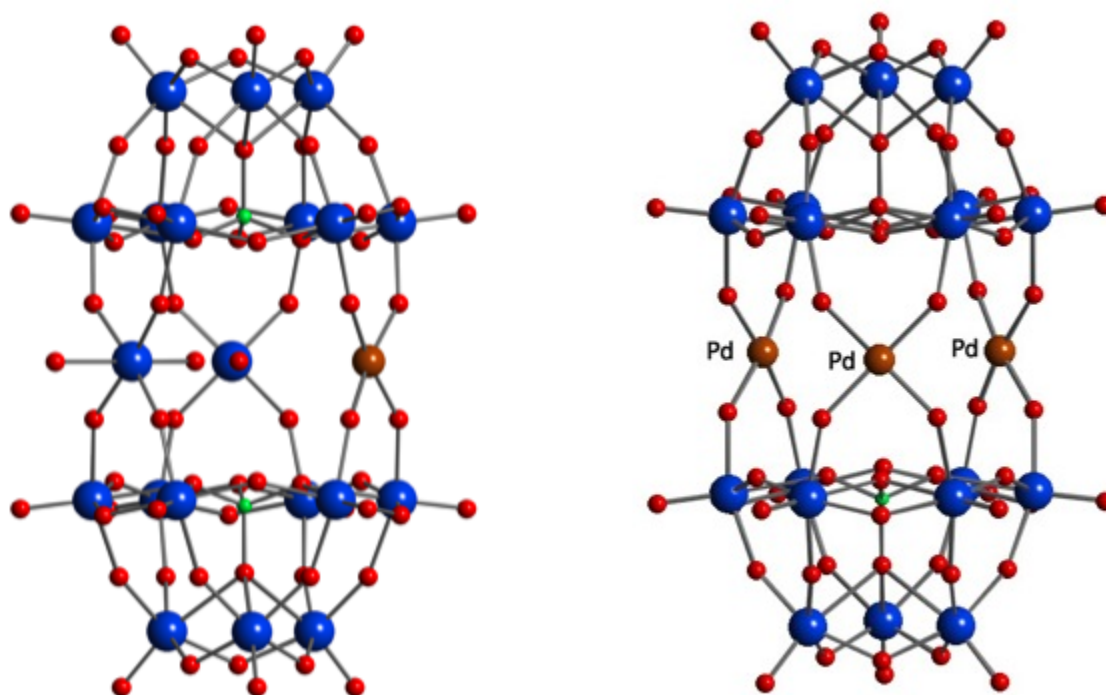


Fig S1: Structural representation of the anions  $[\text{Pd}\{\text{P}_2\text{W}_{20}\text{O}_{70}(\text{H}_2\text{O})_2\}]^{8-}$  anion of **1** (left) and  $[\text{Pd}_3\{\text{PW}_9\text{O}_{34}\}_2]^{12-}$  anion of **2** (right).

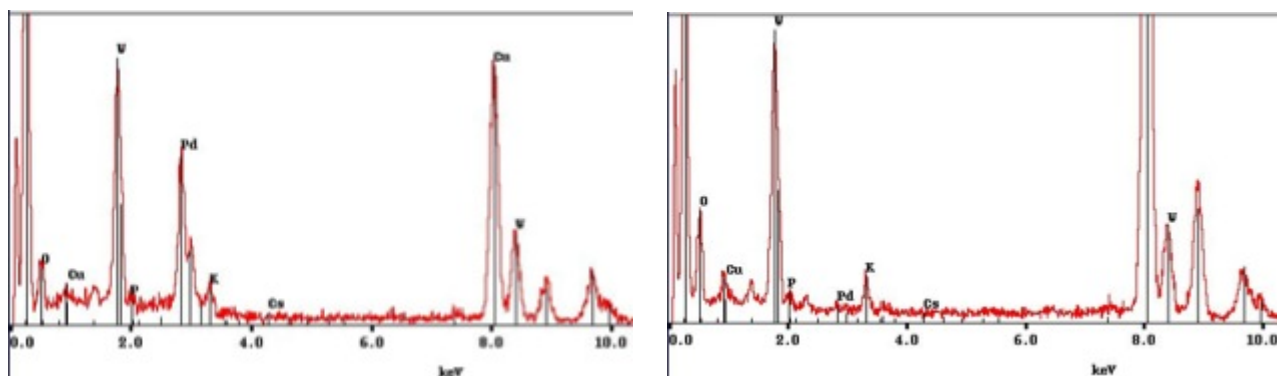


Fig S2: EDX spectra of a single NP of  $\text{Pd}^0$  stabilized by  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  anions (left) and of the amorphous materials around the NPs of  $\text{Pd}^0$  stabilized by  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  anions (right).

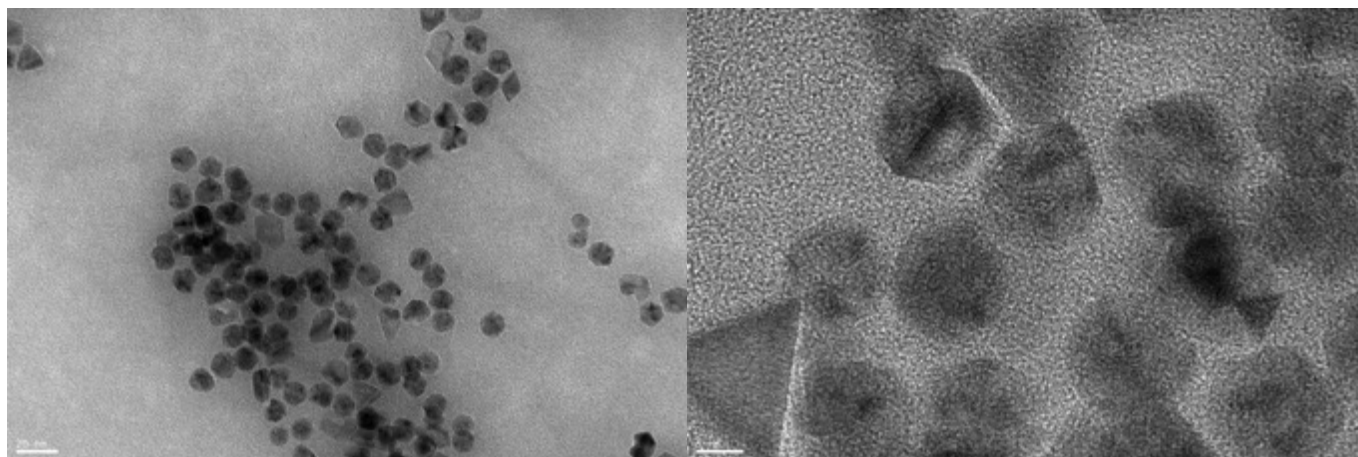


Fig S3: HR TEM micrographs of NPs of Pd<sup>0</sup> stabilized by [PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup> anions at 2 magnifications. The size of the bars in the left corners corresponds to 20 (left) and 5 nm (right) respectively. The picture on the right correspond to the entire micrograph from which the NPs displayed in figure 4 are taken from.

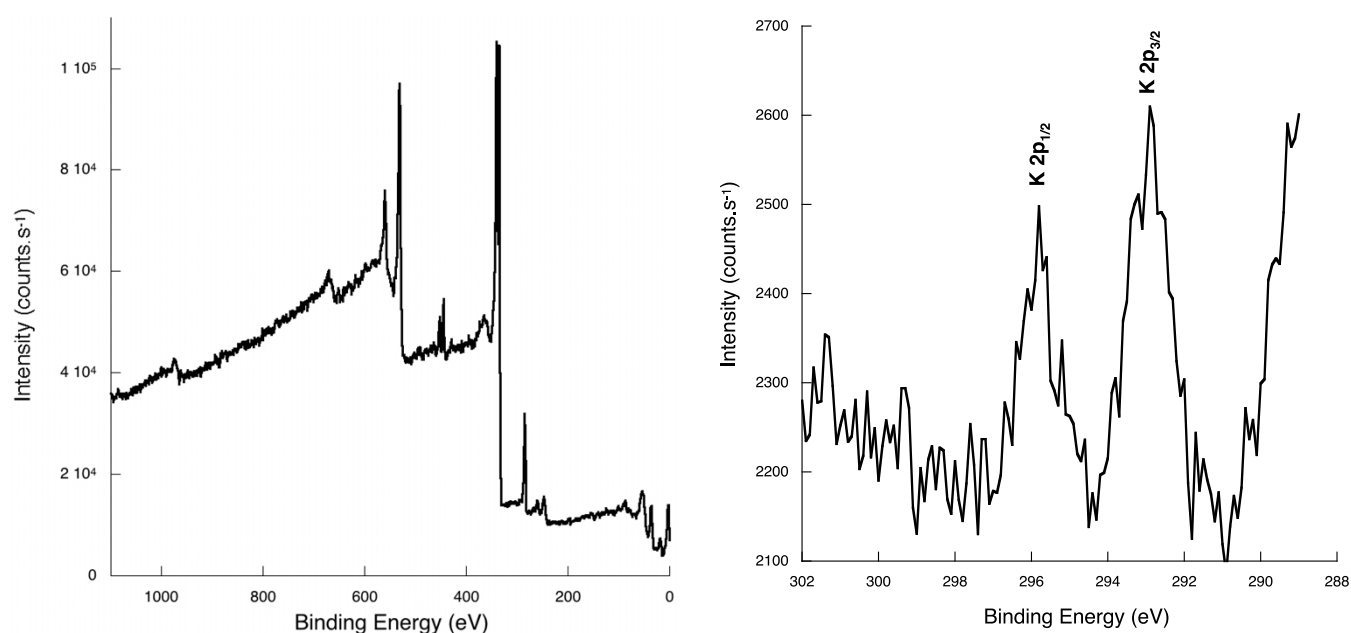


Fig S4: Full XPS spectrum (left) and high resolution K2p spectrum (right) of a solid sample of Pd<sup>0</sup> NPs stabilized by [PW<sub>11</sub>O<sub>39</sub>]<sup>7-</sup> anions prepared by precipitation and filtration of POMs-decorated NPs obtained by reduction of a highly concentrated solution of compound **3** (initial concentration of **3** = 5.10<sup>-3</sup> mol L<sup>-1</sup>).

	<b>Cs<sub>6</sub>K<sub>6</sub>[PdAs<sub>2</sub>W<sub>19</sub>O<sub>67</sub>(H<sub>2</sub>O)]≈7H<sub>2</sub>O</b>
Empirical formula	As <sub>2</sub> Cs <sub>6</sub> K <sub>6</sub> O <sub>75</sub> PdW <sub>19</sub>
Formula weight	5981.45
Crystal system	triclinic
Space group	<i>P</i> <sub>1</sub>
<i>a</i> [Å]	12.5599(6)
<i>b</i> [Å]	12.9532(6)
<i>c</i> [Å]	30.1487(15)
<i>α</i> [°]	80.150(3)
<i>β</i> [°]	84.645(3)
<i>γ</i> [°]	67.299(2)
<i>V</i> [Å <sup>3</sup> ]	4456.2(4)
<i>Z</i>	2
<i>D</i> <sub>calculated</sub> [Mg/m <sup>3</sup> ]	4.458
<i>μ</i> [mm <sup>-1</sup> ]	28.132
<i>F</i> (000)	5124
Crystal size [mm <sup>3</sup> ]	0.15x0.10x0.05
<i>θ</i> range [°]	2.55 – 30.10
	-17 < <i>h</i> < 17
Index ranges	-17 < <i>k</i> < 18
	-42 < <i>l</i> < 42
Refl. collected/unique	25329/16611
Data/restraints/parameters	16611/0/1006
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.040
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.1211
	<i>wR</i> <sub>2</sub> = 0.3851
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1654
	<i>wR</i> <sub>2</sub> = 0.3452
Largest difference peak and hole [e.Å <sup>-3</sup> ]	6.118 and -6.714
CSD deposition numbers	427416

Table S5: crystallographic data for compound Cs<sub>6</sub>K<sub>6</sub>[PdAs<sub>2</sub>W<sub>19</sub>O<sub>67</sub>(H<sub>2</sub>O)]≈7H<sub>2</sub>O which contains the anion of **4**.