

## Supporting information

### Facet-selective adsorption on noble metal crystals guided by electrostatic potential surfaces of aromatic molecules

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**Table S1. Shape distributions of the obtained Pt nanocrystals controlled by different aromatic molecules in Figure 1 and Figure 2.**

	<b>Tetrahedral frequency /%</b>	<b>Cuboctahedral frequency /%</b>	<b>Irregular shape frequency /%</b>	<b>pK<sub>a</sub></b>
<b>Phenol<sup>1</sup></b>	<b>23</b>	<b>66</b>	<b>11</b>	<b>10<sup>a</sup></b>
<b>Catechol<sup>1</sup></b>	<b>67</b>	<b>28</b>	<b>5</b>	<b>9.5<sup>a</sup></b>
<b>Resorcinol<sup>1</sup></b>	<b>35</b>	<b>56</b>	<b>9</b>	<b>9.4<sup>a</sup></b>
<b>Hydroquinone<sup>1</sup></b>	<b>66</b>	<b>28</b>	<b>6</b>	<b>10<sup>a</sup></b>
<b>Pyrogallol<sup>1</sup></b>	<b>73</b>	<b>24</b>	<b>3</b>	<b>10<sup>b</sup></b>
<b>Hydroxyquinol<sup>1</sup></b>	<b>72</b>	<b>22</b>	<b>6</b>	<b>N/A</b>
<b>Phloroglucinol<sup>2</sup></b>	<b>77</b>	<b>17</b>	<b>6</b>	<b>9<sup>c</sup></b>
<b><i>p</i>-nitrophenol<sup>1</sup></b>	<b>4</b>	<b>N/A</b>	<b>N/A</b>	<b>7.1 (phenol with <i>para</i> substituted NO<sub>2</sub>)<sup>a</sup></b>

Gallic acid <sup>2</sup>	42	56	2	4.4 <sup>d</sup>
<i>p</i> -aminophenol <sup>1</sup>	28	64	8	10.3 (phenol with <i>para</i> substituted NH <sub>2</sub> ) 5.5 (aniline with <i>para</i> substituted OH) <sup>a</sup>
<i>p</i> -aminophenol <sup>1</sup> in acid (pH 4)	63	27	10	N/A
Syringol <sup>3</sup>	72	19	9	10 <sup>e</sup>

Note: for all reactions, the volume of final aqueous solution is 5 ml and the concentration mentioned below is final concentration. pH is around 6 for general solutions.

<sup>1</sup> 1 mM of H<sub>2</sub>PtCl<sub>6</sub> mixed with 15 µg/ml of molecule injected with 1 mM of NaBH<sub>4</sub>

<sup>2</sup> 1 mM of H<sub>2</sub>PtCl<sub>6</sub> mixed with 15 µg/ml of molecule injected with 0.5 mM of NaBH<sub>4</sub>

<sup>3</sup> 1 mM of H<sub>2</sub>PtCl<sub>6</sub> mixed with 60 µg/ml of molecule injected with 1 mM of NaBH<sub>4</sub>

References:

<sup>a</sup> Brown, H.C. et al., in Braude, E.A. and F.C. Nachod *Determination of Organic Structures by Physical Methods*, Academic Press, New York, 1955.

<sup>b</sup> Lin, D.; Xing, B. *Environ. Sci. Technol.* **2008**, 42, 7254-7259

<sup>c</sup> Anderson, N. J.; Bolto, B. A.; Eldridge, R. J.; Jackson, M. B. *React. Polym.* **1993**, 19, 87-95.

<sup>d</sup> Wang, S. F.; Chen, X. G.; Hu, Z. D.; Ju, Y. *Biomed. Chromatogr.* **2003**, 17, 306-311.

<sup>e</sup> Ragnar, M.; Lindgren, C. T.; Nilvebrant, N.-O. *J. Wood Chem. Technol.* **2000**, 20, 277-305.

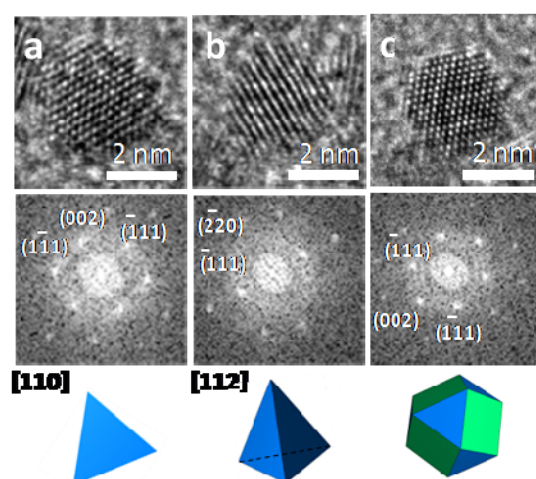


Figure S1. HRTEM images, the corresponding Fourier transform patterns and geometrical models of (a) a Pt tetrahedron imaged along [110], (b) a Pt tetrahedron imaged along [112] and (c) a Pt cuboctahedron.

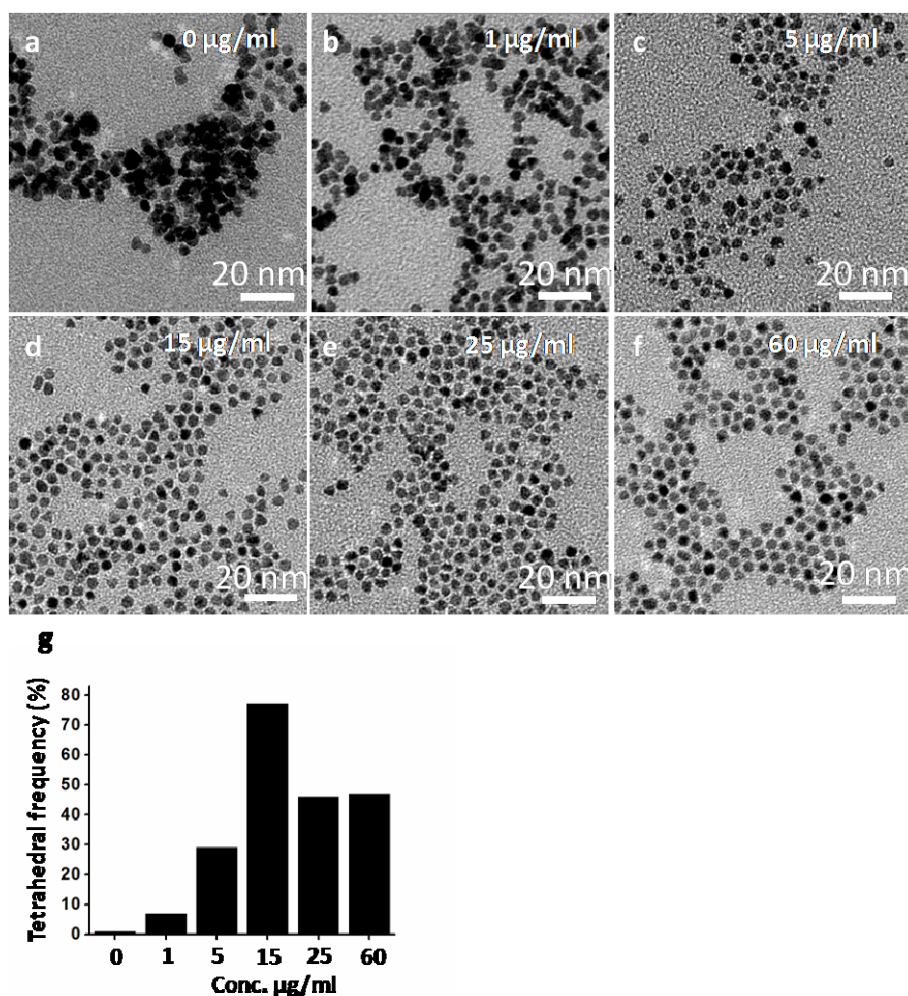


Figure S2. TEM images of Pt nanocrystals as a function of the concentration of phloroglucinol: (a) blank control (0  $\mu\text{g/ml}$ ), (b) 1  $\mu\text{g/ml}$ , (c) 5  $\mu\text{g/ml}$ , (d) 15  $\mu\text{g/ml}$ , (e) 25  $\mu\text{g/ml}$  and (f) 60  $\mu\text{g/ml}$ . (g) Pt tetrahedral frequency as a function of the concentration of phloroglucinol. The synthetic condition is kept the same in all reactions except for the concentration of phloroglucinol.

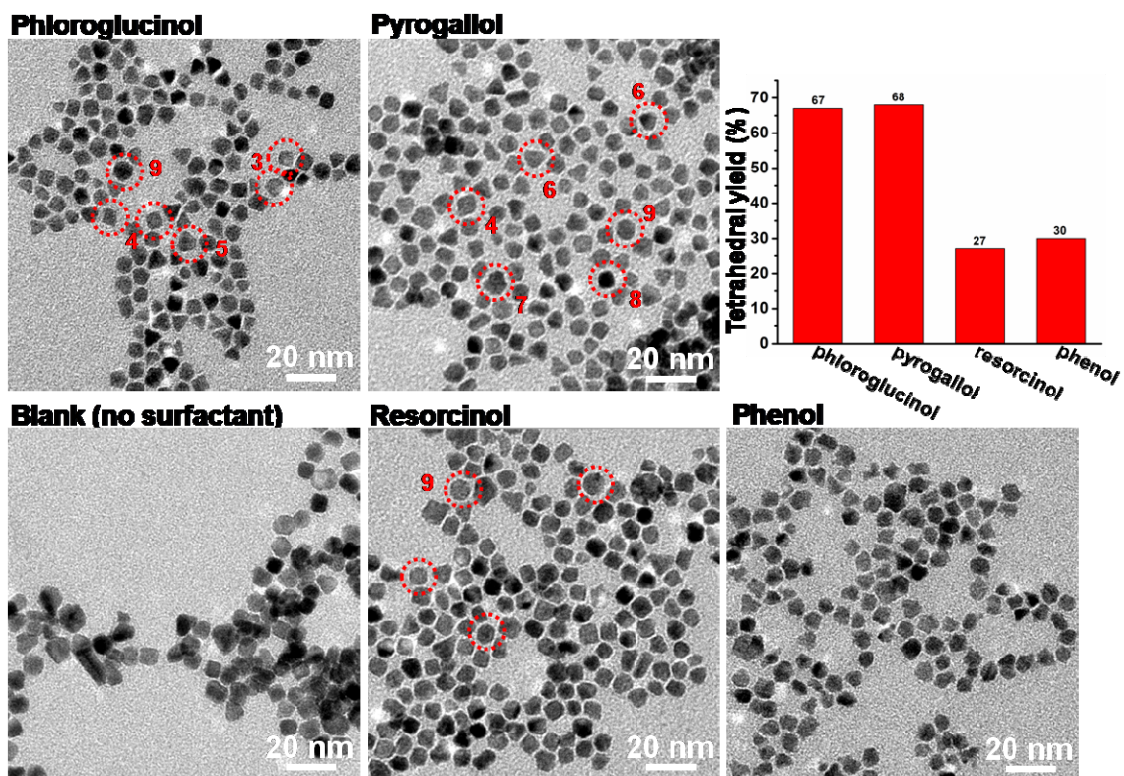


Figure S3. TEM images of Pt nanocrystals controlled with and without aromatic molecules. 1 mM  $K_2PtCl_4$  mixed with 0.5 mM ascorbic acid and 15  $\mu\text{g/ml}$  aromatic molecules were injected with 0.5 mM  $NaBH_4$ , reacting for 2 hours. The total volume of all reaction solutions is 5 ml. The concentrations indicated are all final concentration. The HRTEM images of the nanocrystals marked by red dashed circle can be found in Figure S4, demonstrating their corresponding shape.



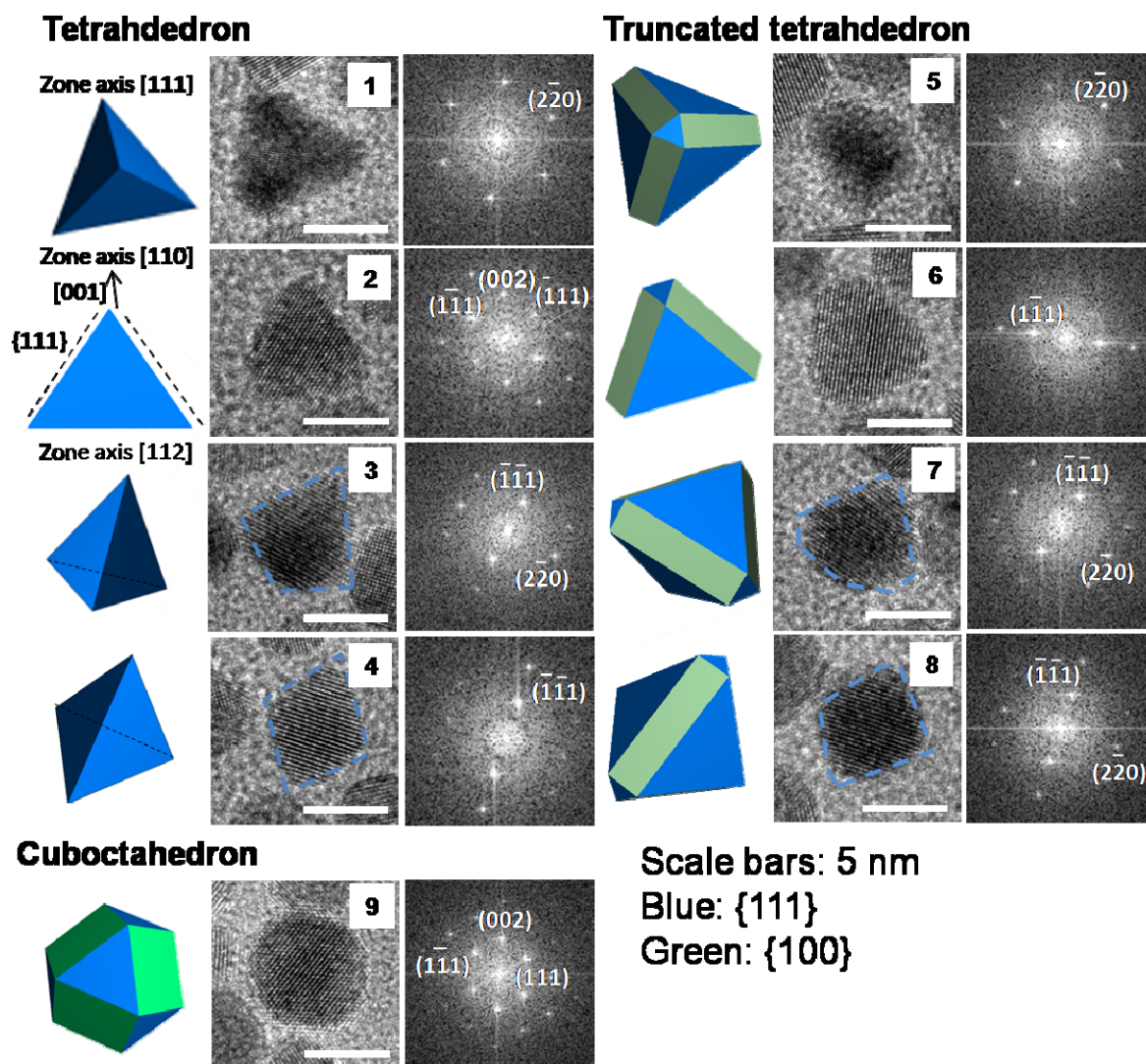


Figure S4. HRTEM images of Pt tetrahedra (imaged along different directions), truncated tetrahedra (imaged along different directions) and cuboctahedron.

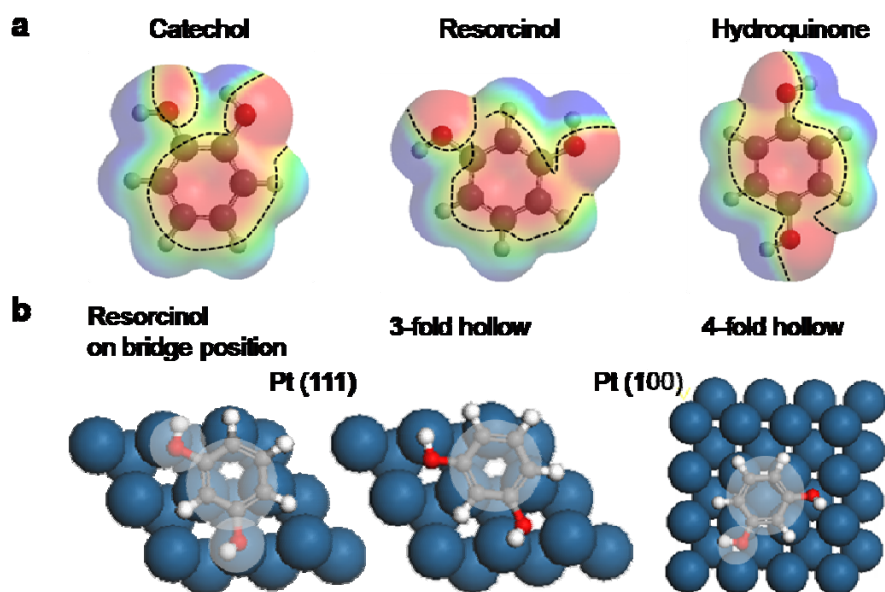
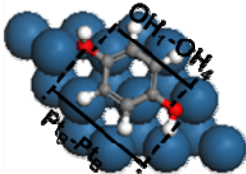




Figure S5. (a) Depiction of the shape of the red (negative) region of electrostatic potential surfaces of catechol, resorcinol and hydroquinone. (b) The possible adsorption geometries of resorcinol on Pt(111) and Pt(100) lattice. The grey circles indicate the potential binding sites of molecules on Pt surfaces.

**Table S2. Geometric matching of phenolics on Pt(111) surface**

	Configuration on Pt(111)	Epitaxial relation
<b>Hydroquinone<sup>1</sup></b> Ring: Bridge(30) 2 OH: Bridge		<b>Pt<sub>B</sub>-Pt<sub>B</sub>: 6.3 Å</b> <b>OH<sub>1</sub>-OH<sub>4</sub>: 6.0 Å</b>
<b>Phloroglucinol<sup>2</sup></b> Ring: Bridge(30) 3 OH: Top		<b>Pt<sub>T</sub>-Pt<sub>T</sub>: 5.5 Å</b> <b>OH<sub>1</sub>-OH<sub>3</sub>: 5.3 Å</b>

<b>Pyrogallol<sup>3</sup></b> Ring: Bridge(30) 2 OH: Top 1 OH: Bridge		<b>Pt<sub>T</sub>-Pt<sub>T</sub> : 5.5 Å</b> <b>OH<sub>1</sub>-OH<sub>3</sub> : 5.0 Å</b> <b>Pt<sub>B</sub>-Pt<sub>T</sub> : 3.1 Å</b> <b>OH<sub>1</sub>-OH<sub>2</sub> : 2.8 Å</b>
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Note: the bond length and angle of the molecular structures are based on the experimental or calculated crystal structures of molecules.

References:

<sup>1</sup> Ermer, O. *Helv. Chim. Acta* **1991**, 74, 1339-1351.

<sup>2</sup> Maartmann-Moe, K. *Acta Crystallogr.* **1965**, 19, 155-157.

<sup>3</sup> Vedernikova, I.; Salahub, D.; Proynov, E. *J. Mol. Struct.: THEOCHEM* **2003**, 663, 59-71.

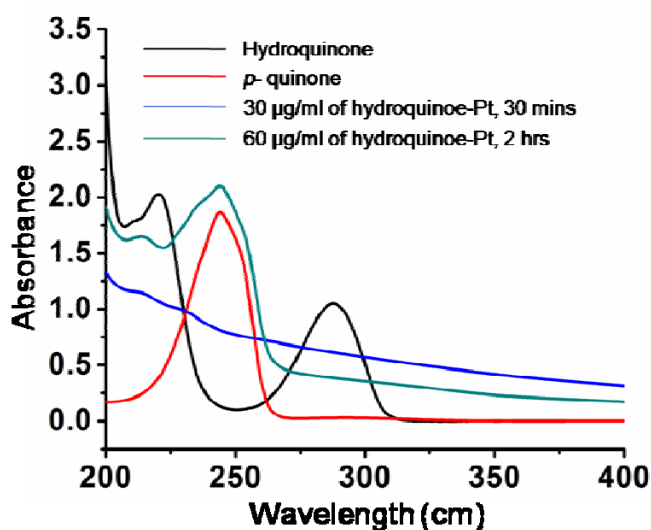


Figure S6. UV-vis adsorption of hydroquinone (30 µg/ml), *p*-quinone (30 µg/ml) and hydroquinone-Pt nanocrystals solutions (Blue: 30 µg/ml of hydroquinone-synthesized Pt nanocrystals solution reacting for 30 minutes; green: 60 µg/ml of hydroquinone-synthesized Pt nanocrystals solution reacting for more than 2 hours). The spectrum of of hydroquinone (30 µg/ml) -Pt, 30 mins (the reaction condition is similar to Pt tetrahedra synthesis) showing no characteristic peak of *p*-quinone indicates that hydroquinone did not oxidized to *p*-quinone in the reaction. However, as shown in the spectrum of 60 µg/ml of hydroquinone –Pt, 2 hrs, hydroquinone oxidized and formed *p*-quinone as higher concentration and long reaction time is

performed, indicating that excessive hydroquinone which did not bind on metal surface would oxidize. The UV-vis adsorption was conducted by DU800 UV-vis spectrometer.

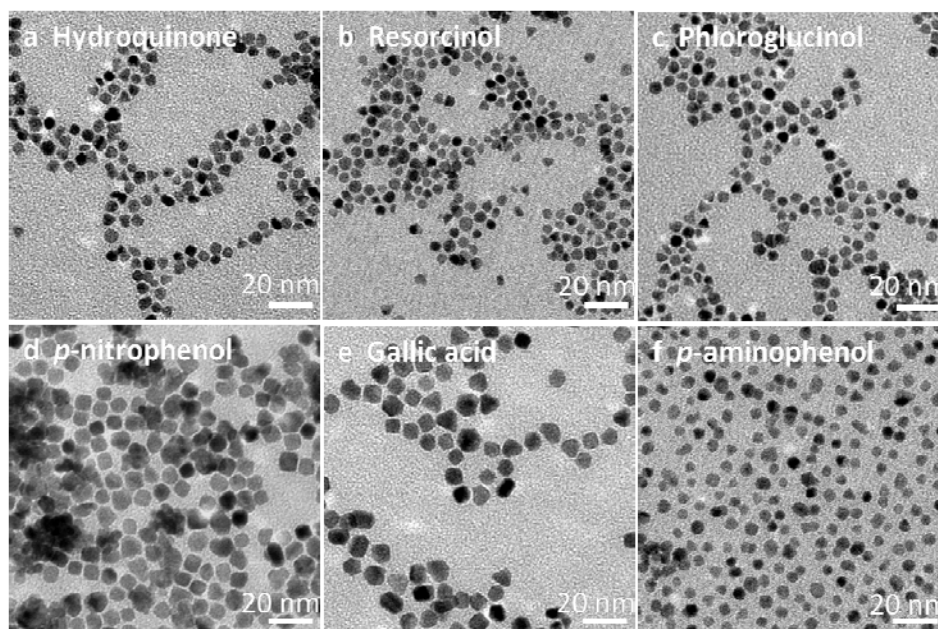


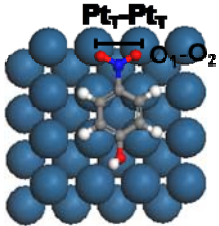
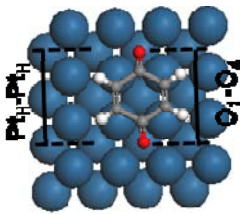
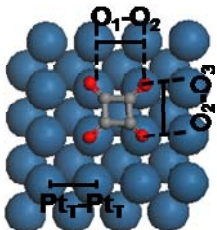
Figure S7. TEM images of aromatic molecules control synthesis of Pt nanocrystals with the addition of ascorbic acid: 1 mM of  $\text{H}_2\text{PtCl}_6$  mixed with 0.5 mM of ascorbic acid and 12  $\mu\text{g}/\text{ml}$  of molecules injected with 2 mM  $\text{NaBH}_4$ , indicating the molecular facet binding selectivity is not affected by changing the reaction condition.

**Table S3. Tetrahedral yields of phenolics control synthesis of Pt nanocrystals in Figure S4**

	<b>Tetrahedral frequency /%</b>	<b>Other products</b>
<b>Hydroquinone</b>	<b>67</b>	
<b>Resorcinol</b>	<b>48</b>	
<b>Phloroglucinol</b>	<b>63</b>	
<b><i>p</i>-nitrophenol</b>	<b>N/A</b>	<b>Cube: 66%</b> <b>Cuboctahedron: 16%</b> <b>Irregular: 18%</b>

Gallic acid	20	Cube: 18% Cuboctahedron: 58%
<i>p</i> -aminophenol	27	

**Table S4. Geometric matching of organic molecules on Pt(100) surface**

	Configuration on Pt(100)	Epitaxial relation
<b><i>p</i>- nitrophenol<sup>1</sup></b> Ring: 4 fold-hollow 2 O: Top 1 OH: hollow		<b>Pt<sub>T</sub>-Pt<sub>T</sub> : 2.8 Å</b> <b>O<sub>1</sub>-O<sub>2</sub> : 2.2 Å</b>
<b><i>p</i>- quinone<sup>2</sup></b> Ring: 4 fold-hollow 2 O: hollow		<b>Pt<sub>H</sub>-Pt<sub>H</sub> : 5.5 Å</b> <b>O<sub>1</sub>-O<sub>4</sub> : 5.3 Å</b>
<b>Squaric acid<sup>3</sup> (dianion)</b> Ring: hollow 4 O: Top		<b>Pt<sub>T</sub>-Pt<sub>T</sub> : 2.8 Å</b> <b>O<sub>1</sub>-O<sub>2</sub> : 3.2 Å</b> <b>O<sub>2</sub>-O<sub>3</sub> : 3.1 Å</b>

Note: the bond length and angle of the molecular structures are based on the experimental or calculated crystal structures of molecules.

References:

<sup>1</sup> Coppens, P.; Schmidt, G. M. J. *Acta Crystallogr.* **1965**, *18*, 654-663.

<sup>2</sup> Trotter, J. *Acta Crystallogr.* **1960**, *13*, 86-95.

<sup>3</sup> Braga, D.; Maini, L.; Prodi, L.; Caneschi, A.; Sessoli, R.; Grepioni, F. *Chem. – A Eur. J.* **2000**, *6*, 1310-1317.



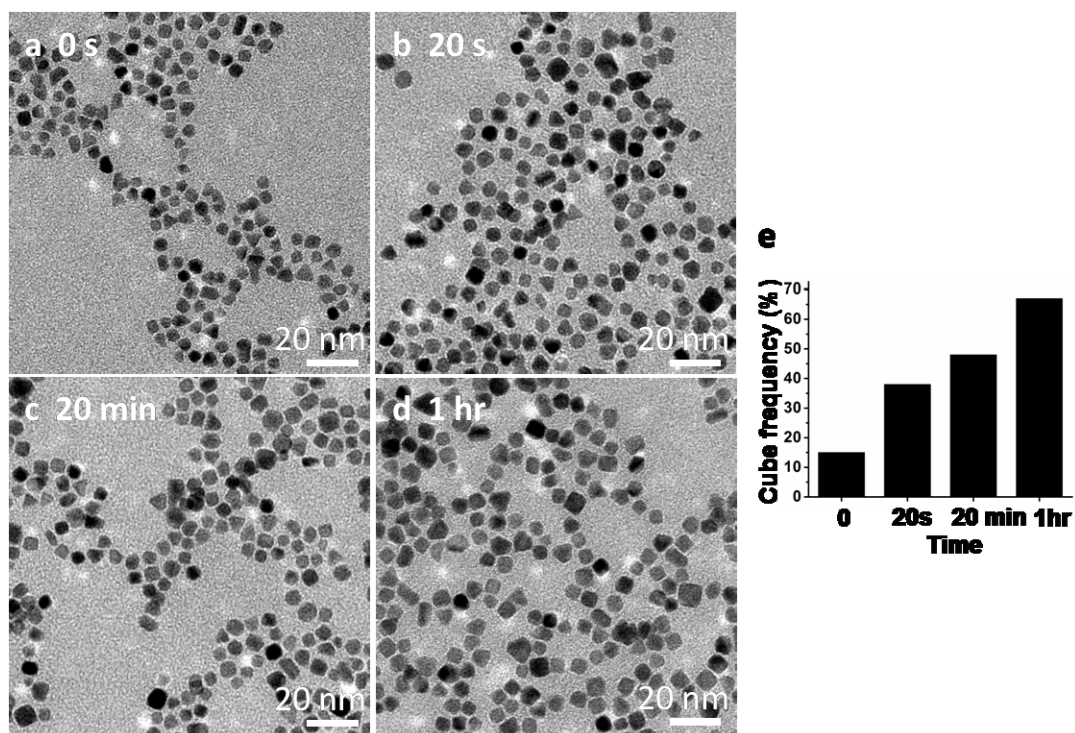


Figure S8. Shape evolution of Pt cubes controlled by *p*-quinone. (a - d) TEM images of nanocrystals obtained from the reaction over time after introducing *p*-quinone: (a) 0 second, (b) 20 seconds, (c) 20 minutes and (d) 1 hour. (e) Pt cubes population as a function of reaction time.

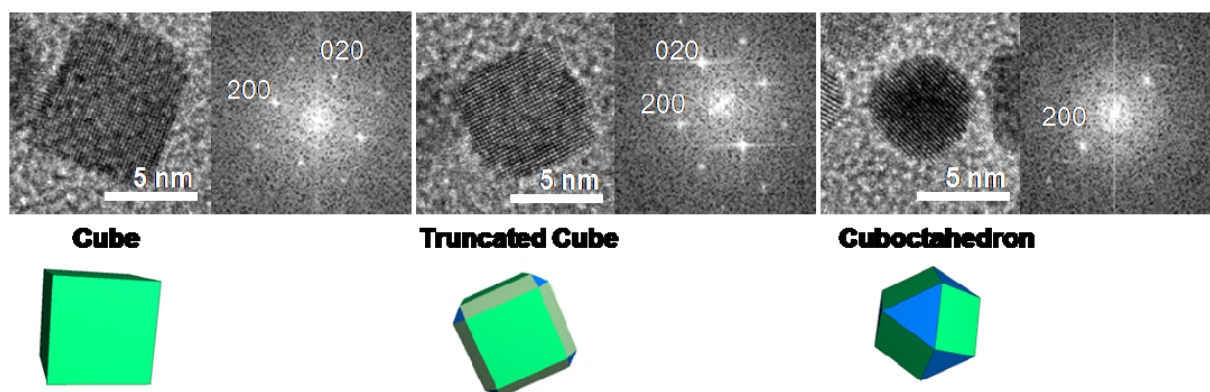


Figure S9. HRTEM images of Pt nanocrystals with the shape of cube, truncated cube and cuboctahedron obtained in the *p*-quinone control synthesis and their corresponding Fourier transform patterns.

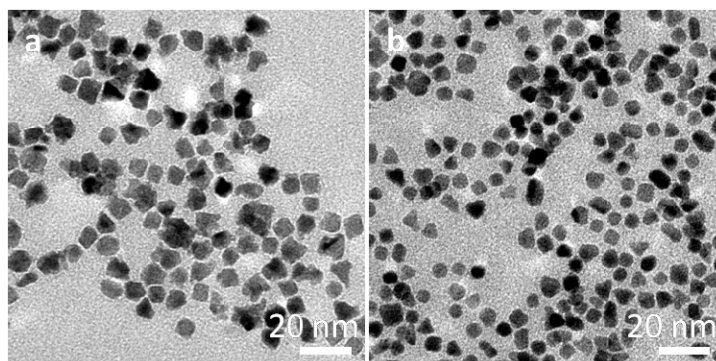


Figure S10. TEM image of the obtained nanocrystals from the control reactions: (a) 1 mM of  $\text{H}_2\text{PtCl}_6$  mixed with 0.5 mM ascorbic acid and 8  $\mu\text{g/ml}$  of *p*-quinone, injected with 0.5 mM  $\text{NaBH}_4$ . (b) TEM image of nanocrystals obtained from the blank control reaction (without *p*-quinone).

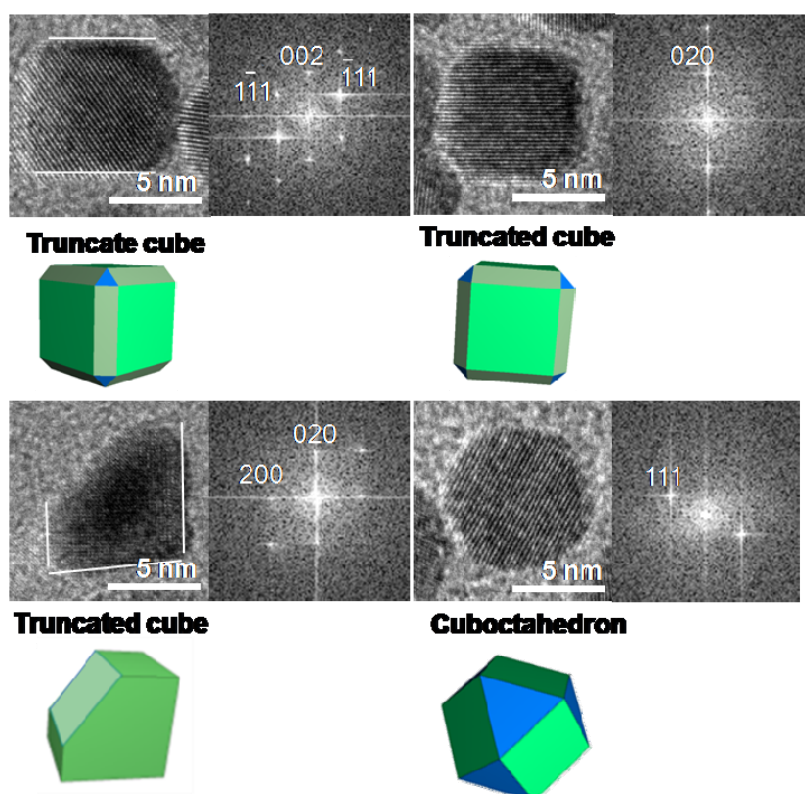


Figure S11. HRTEM images, the corresponding Fourier transform patterns and schematic models of truncated cube and cuboctahedron observed in the squaric acid controlled synthesis of Pt nanocrystals.

**Table S5 The energies of highest occupied molecular orbital ( $\epsilon_{\text{HOMO}}$ ) of small molecules calculated at density functional B3LYP/ 6-31G\* level (Spartan) and DFT-PBE (VASP), respectively. Work functions of different metal surfaces from references and obtained via DFT-PBE calculations are given below, respectively.**

<b>Molecule</b>	<b>HOMO (BLYP3) (eV)</b>	<b>HOMO (DFT-PBE) (eV)</b>
Terephthalic acid	-7.4	-7.15
<i>p</i> -quinone	-7.4	-6.64
<i>p</i> -nitrophenol	-6.9	-6.36
Benzene	-6.7	-6.36
Squaric acid	-6.5	-5.83
Phenol	-6.0	-5.96
Gallic acid	-6.0	-5.83
Resorcinol	-5.8	-5.66
		$E_{\text{F}}$ of Pt (111): -5.77 Set $E_{\text{VAC}}$ as 0
Phloroglucinol	-5.8	-5.64
		$E_{\text{F}}$ of Pd (111):-5.59
Catechol	-5.6	-5.43
Pyrogallol	-5.6	-5.51
Hydroquinone	-5.4	-5.34
Syringol	-5.3	-5.39
Hydroxyquinol	-5.2	-4.86
<i>p</i> -aminophenol	-5.0	-4.71
<b>Metal surface</b>	<b>Work function (ref.)</b>	<b>Work function (<math>\Phi</math>) (DFT; PBE)</b>
Pt(111)	6.1 <sup>1</sup> /5.7 <sup>2</sup> /5.93 <sup>3</sup>	5.77
Pt(100)	5.84 <sup>3</sup>	5.71
Pd(111)	5.6 <sup>2</sup> /5.5 <sup>4</sup>	5.59
Pd(100)	5.3 <sup>4</sup>	5.25

Note: all the density functional theory (DFT) calculations were performed with Vienna Ab initio Simulation Package (VASP)<sup>5</sup> utilizing self-consistent to solve the Kohn-Sham one electron equations. The wave function was expanded with a set of plane wave set whose cutoff energy is 700 eV. The Perdew-Burke Ernzerhof (PBE)<sup>6</sup> flavor of general gradient approximation was employed describing the exchange and correlation of electrons. The Brillouin Zone was sampled with 3×3×1 Monkhorst and Pack mesh<sup>7</sup>. The Pt and Pd surfaces were modeled employing a slab model containing 6 layers of metal atoms and a 4×4 supercell in each layer. An 11.9 Å thick vacuum layer was introduced to render the interaction between two metal layers. The top three layers are fully relaxed to simulate the surface while the bottom 3 layers are kept fixed to simulate the bulk utilizing the calculated equilibrium bulk lattice constant. The lattice constants of Pt and Pd are calculated to be 3.99 Å and 3.97 Å respectively, which are in agreement with the experimental value. As this forms an asymmetric model, the dipole correlation was introduced to the all the work function calculations. The isolated organic molecules are modeled in the

12Å×12Å×12Å supercell. Their HOMO and LUMO can be gained from the calculation of their energy eigenvalues by VASP code. The work function is calculated by subtracting Fermi level from the electrostatic potential within the vacuum layer, which represents vacuum level.

#### References:

- <sup>1</sup> Derry, G. N.; Ji-Zhong, Z. *Phys. Rev. B* **1989**, *39*, 1940-1941.
- <sup>2</sup> Michaelson, H. B. *J. Appl Phys.* **1977**, *48*, 4729-4733.
- <sup>3</sup> Nieuwenhuys, B. E.; Sachtler, W. M. H. *Surf. Sci.* **1973**, *34*, 317-336.
- <sup>4</sup> Methfessel, M.; Hennig, D.; Scheffler, M. *Phys. Rev. B* **1992**, *46*, 4816-4829.
- <sup>5</sup> Kresse, G.; Hafner, J. *Phys. Rev. Lett.* **1993**, *47*, 558-561
- <sup>6</sup> Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868
- <sup>7</sup> Monkhorst, H.J.; Pack, J.D. *Phys. Rev. B* **1976**, *13*, 5188-5192

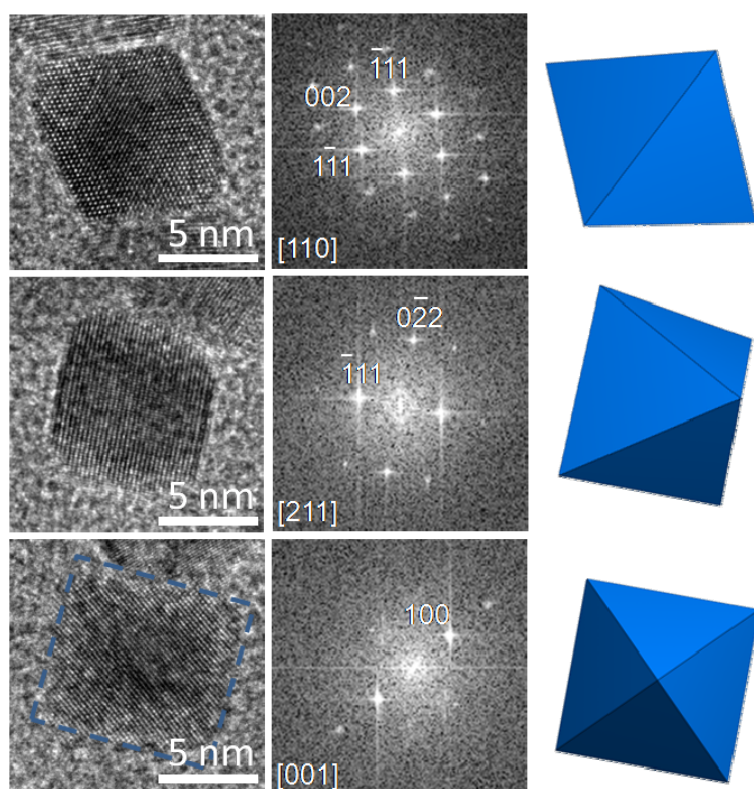


Figure S12. HRTEM images, the corresponding Fourier transform patterns and schematic models of Pd octahedrons recorded along different directions in the hydroquinone controlled synthesis of Pd octahedrons.



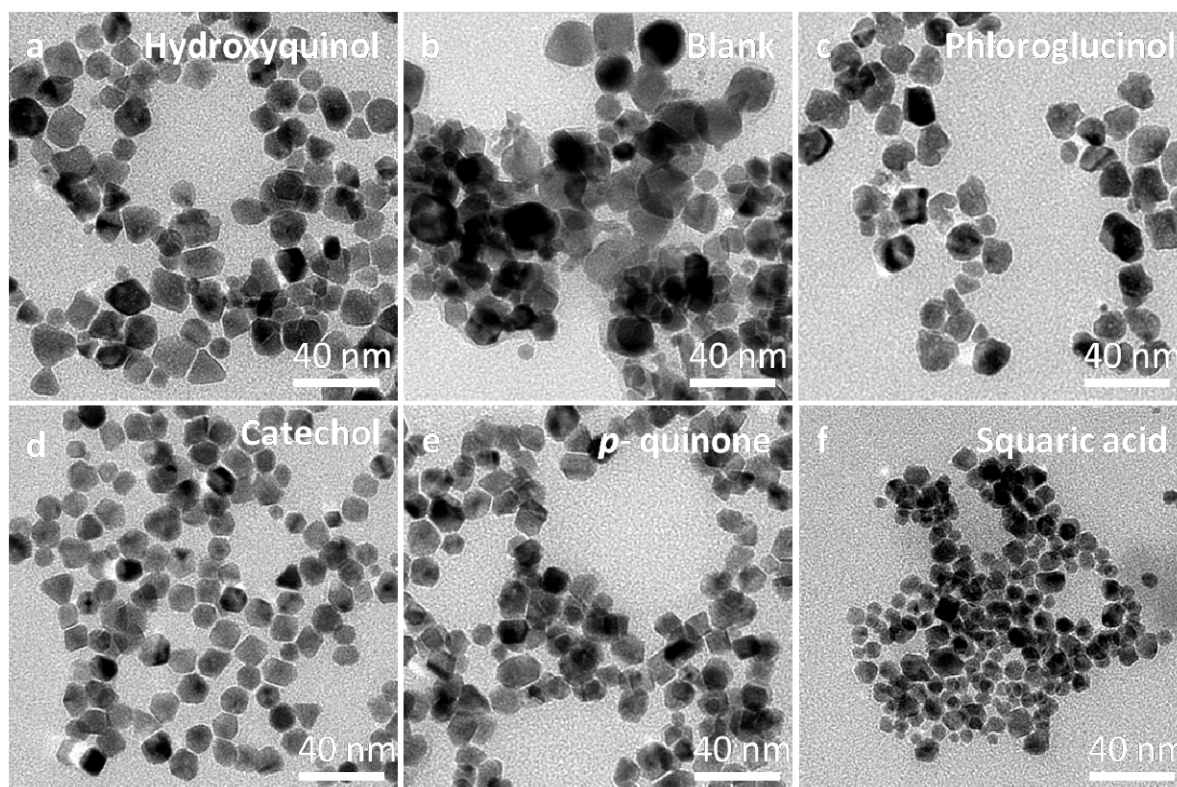


Figure S13. Control experiments of Pd nanocrystals synthesized by other organic molecules than Pd(111) and Pd(100) binding molecules. TEM images of the obtained Pd nanocrystals in the presence of 3 mg of hydroxyquinol (a); no surfactant (b); 3 mg of phloroglucinol (c); 3 mg of catechol (d); 3 mg of *p*-quinone (e); 6 mg of squaric acid (f).

**Table S6 Geometric matching of terephthalic acid on Pd(100) surface**

	Configuration on Pd(100)	Epitaxial relation
<b>Terephthalic acid<sup>1</sup></b> Ring: 4 fold-hollow 4 O: Top		Pd <sub>T</sub> -Pd <sub>T</sub> (1): 8.3 Å Pd <sub>T</sub> -Pd <sub>T</sub> (2): 2.8 Å O <sub>1</sub> -O <sub>2</sub> : 7.0 Å O <sub>2</sub> -O <sub>3</sub> : 2.2 Å

Note: the bond length and angle of the molecular structures are based on the previous report.

Reference:

<sup>1</sup> Bailey, M.; Brown, C. J. *Acta Crystallogr.* **1967**, 22, 387-391.



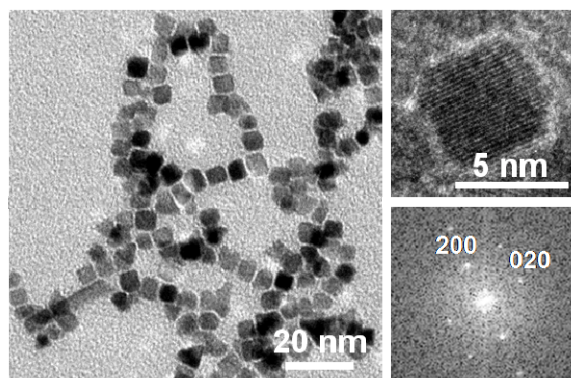


Figure S14. TEM image of Pt cubes with a yield of 73 % controlled by terephthalic acid. Pt nanocrystals were synthesized in the reaction with 15  $\mu\text{g/ml}$  terephthalic acid, 2.4 mM  $\text{K}_2\text{PtCl}_4$ , 2 mM ascorbic acid and 1 mM  $\text{NaBH}_4$  in the solution containing 3.5 ml DMF and 1.5 ml water, reacting in 60°C oil bath for two hours.