

Supporting Information**Block Copolymer Templated Synthesis of PtIr Bimetallic Nanocatalysts for the Formic Acid Oxidation Reaction**

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The FEI Tecnai Osiris TEM instrument was used for transmission electron microscopy and energy dispersive X-ray mapping. Magnification calibration was performed using an automated procedure with a standardized Au-Pd grating. To ensure accuracy in the determination of lattice parameters by selected area electron diffraction, samples were studied with the same imaging conditions as those for an Al calibration standard. Typically, the data images and/or diffraction patterns of experimental samples are obtained followed by the study of the polycrystalline Al standard under the same electrical and magnetic conditions (i.e. the same lens current, high voltage, and magnification/camera length) to confirm the calibration accuracy. From a typical SAED image, the lattice parameters are assigned as per the below d-spacings for Al.

Miller Indices (hkl)	Lattice Spacing (Å)	Normalized Intensity	Lattice Constant (Å)
111	2.338	100	4.05
200	2.024	47	4.048
220	1.431	22	4.047
311	1.221	24	4.0489
222	1.169	7	4.0495
400	1.0124	2	4.0496
331	0.9289	8	4.049

Following the assignment of the d-spacings, a calibration constant (K) is calculated using the formula $K = S \times d$. K encompasses the wavelength of the electron beam, camera length and the associated variation in the crystallographic data, S represents the diameter of a diffraction ring in centimeters and d is the interplanar spacing in angstroms. The tolerance level for variation in the values for calibration constant for the first five lines is 1%. The imaging software is integrated with this calibration data to standardize the reciprocal readings of lattice spacing information acquired from FFT interpretations.

Table S1: Brief comparison of catalytic activity for formic acid oxidation reported for several binary and ternary systems.

Binary System	Catalytic Activity
PdPt ^{S1}	A mass activity of 1200 A/g was produced for the I ₁ peak for a nanoporous alloy with a composition of Pd ₈₀ Pt ₂₀ .
PdCu ^{S2}	The I ₁ peak was used for comparison and a current density value of ~ 0.45 mA/cm ² was reported for a layered thin films of PdCu.
PtRu ^{S3}	The catalytic activity of Pt ₇ Ru ₃ nanowires were evaluated for formic acid oxidation. A current density of ~1.5 mA/cm ² was reported.
PtRuFe ^{S3}	The I ₁ peak demonstrated a current density of ~2.1 mA/cm ² for a reported composition of Pt ₇ Ru _{1.5} Fe _{1.5} .
PtFe ^{S3}	A current density of ~0.55 mA/cm ² was reported for the I ₁ peak produced from Pt ₇ Fe ₃ nanowires.
PdNi ^{S4}	A composition of Pd ₈₁ Ni ₁₉ showed a current density of ~1.75 mA/cm ² for the I ₁ peak.
PdNiCu ^{S4}	A trimetallic catalyst of Pd ₅₇ Ni ₁₃ Cu ₃₀ exhibited a current density of 3.3 mA/cm ² for the I ₁ peak.
FePt ^{S5}	The I ₁ peak was used for comparison and a current density of 104 mA/cm ² was produced from the best preforming catalyst, Fe ₄₂ Pt ₅₈ .
PdPt ^{S6}	Formic acid oxidation was assessed using cyclic voltammetry and chronoamperometry. The I ₁ peak was used for comparison and a mass activity value of 0.0023 A/g was reported for Pd ₁₀₀ Pt ₀ /CNT.
PtAu ^{S7}	Formic acid electrooxidation was characterized by mass activity values and 8000 A/g was reported for the I ₃ peak of a NPG-Pt ₁ Au ₂ catalyst.
PtPb ^{S8}	A mass activity value of 1330 A/g for the I ₁ peak of Pd-Pt catalyst was compared and reported to monometallic Pd and Pt for formic acid oxidation. The current density was normalized to catalyst loading and particle size was also used to characterize activity.
FePt ^{S9}	Formic acid oxidation was catalyzed by Fe _x Pt _{100-x} catalysts and a current density of 0.5 mA/cm ² was reported for the I ₁ peak. Voltammetric currents were normalized to the Pt active surface area. The best preforming catalyst was considered to be the Fe ₂₀ Pt ₈₀ catalyst.
PtRu ^{S10}	Nanocrystals of Pt-Ru were studied catalytically by formic acid oxidation. A current density of ~5 mA/cm ² and a mass activity of ~140 A/g were reported and compared to that of a commercial Pt-Ru standard.

Table S2. SFM-estimated height, FWHM, and periodicity for each PS-*b*-P4VP template cast onto ITO substrates. Dimensions are estimated from the mean of 5 sets of 3 aligned micelles in the SFM images.

Dimension	PS- <i>b</i> -P4VP diblock copolymer template ^a - SFM measured dimensions in nm. (Std. Dev.)	
	PS ₁₃₉₂ - <i>b</i> -P4VP ₄₇₁	PS ₅₅₂ - <i>b</i> -P4VP ₁₇₄
FWHM ^b	54 (5)	35 (5)
Height	26 (3)	14 (3)
Periodicity	101 (8)	63 (8)

^a – *n* and *m* represent the average number of repeat units of the PS and P4VP blocks, respectively.

^b – full width at half maximum.

Table S3. Comparison of twenty compositionally tuned particle clusters synthesized from immersion into 100 mM H₂SO₄ with 10 mM [H₂IrCl₆ + H₂PtCl₆].

Pt : Ir molar ratio in immersion bath	NP and Cluster Parameters	PS _n - <i>b</i> -P4VP _m Diblock copolymer template ^a and TEM estimated dimensions (Std. Dev.)	
		PS ₁₃₉₂ - <i>b</i> -P4VP ₄₇₁	PS ₅₅₂ - <i>b</i> -P4VP ₁₇₄
10 : 0	NP Diameter ^b	10 ± 4 nm	6 ± 3 nm
	NPs per Cluster ^c	2 ± 1	7 ± 3
	Periodicity ^d	116 ± 7 nm	56 ± 9 nm
	Stoichiometry Estimated by XPS	Pt ₁₀₀ Ir ₀	Pt ₁₀₀ Ir ₀
9.75 : 0.25	NP Diameter ^b	6 ± 2 nm	6 ± 3 nm
	NPs per Cluster ^c	7 ± 4	4 ± 2
	Periodicity ^d	145 ± 14 nm	71 ± 11 nm
	Stoichiometry Estimated by XPS	Pt ₉₇ Ir ₃	Pt ₉₇ Ir ₃
9.5 : 0.5	NP Diameter ^b	4 ± 1 nm	6 ± 2 nm
	NPs per Cluster ^c	6 ± 3	4 ± 2
	Periodicity ^d	144 ± 19 nm	74 ± 11 nm
	Stoichiometry Estimated by XPS	Pt ₉₁ Ir ₉	Pt ₇₉ Ir ₂₁
9.0 : 1.0	NP Diameter ^b	12 ± 3 nm	7 ± 2 nm
	NPs per Cluster ^c	2.4 ± 1.2	1.4 ± 0.7
	Periodicity ^d	122 ± 14 nm	54 ± 10 nm
	Stoichiometry Estimated by XPS	Pt ₆₀ Ir ₄₀	Pt ₅₈ Ir ₄₂
8.0 : 2.0	NP Diameter ^b	13 ± 5	9 ± 1
	NPs per Cluster ^c	1.6 ± 1.0	1.8 ± 1.2
	Periodicity ^d	116 ± 14 nm	45 ± 7 nm
	Stoichiometry Estimated by XPS	Pt ₃₃ Ir ₆₇	Pt ₃₆ Ir ₆₄
7.5 : 2.5	NP Diameter ^b	11 ± 3	9 ± 1
	NPs per Cluster ^c	1.4 ± 0.9	1.2 ± 0.5
	Periodicity ^d	120 ± 10 nm	45 ± 5 nm
	Stoichiometry Estimated by XPS	Pt ₃₆ Ir ₆₄	Pt ₂₈ Ir ₇₂
7.0 : 3.0	NP Diameter ^b	9 ± 1	9 ± 1
	NPs per Cluster ^c	2.4 ± 1.1	1.2 ± 0.5
	Periodicity ^d	128 ± 7 nm	49 ± 8 nm
	Stoichiometry Estimated by XPS	Pt ₁₈ Ir ₈₂ ^δ	Pt ₂₀ Ir ₈₀
5.0 : 5.0	NP Diameter ^b	11 ± 3	10 ± 1
	NPs per Cluster ^c	2.2 ± 1.3	1.2 ± 0.4
	Periodicity ^d	112 ± 15 nm	49 ± 8 nm
	Stoichiometry Estimated by XPS	Pt ₁₉ Ir ₈₁	Pt ₁₆ Ir ₈₄
2.4 : 7.6	NP Diameter ^b	11 ± 3	8 ± 1
	NPs per Cluster ^c	1.5 ± 0.7	1.2 ± 0.6
	Periodicity ^d	111 ± 18 nm	55 ± 8 nm
	Stoichiometry Estimated by XPS	Pt ₁₈ Ir ₈₂ ^γ	Pt ₁₁ Ir ₈₉
0 : 10	NP Diameter ^b	13 ± 5 nm	10 ± 4 nm
	NPs per Cluster ^c	n/a*	n/a*
	Periodicity ^d	123 ± 13 nm	66 ± 12 nm
	Stoichiometry Estimated by XPS	Pt ₀ Ir ₁₀₀	Pt ₀ Ir ₁₀₀

^a *n* and *m* represent the average number of repeat units of the PS and P4VP blocks, respectively. ^b Average of 100 particles. ^c Average of 25 clusters. ^d Average of 15 clusters. ^δ Pt₁₈Ir₈₂ estimated stoichiometry from the 7.0:3.0 bath. ^γ Pt₁₈Ir₈₂ estimated stoichiometry from the 2.4:7.6 bath. * Continuous metal phase present in nanoring formation.

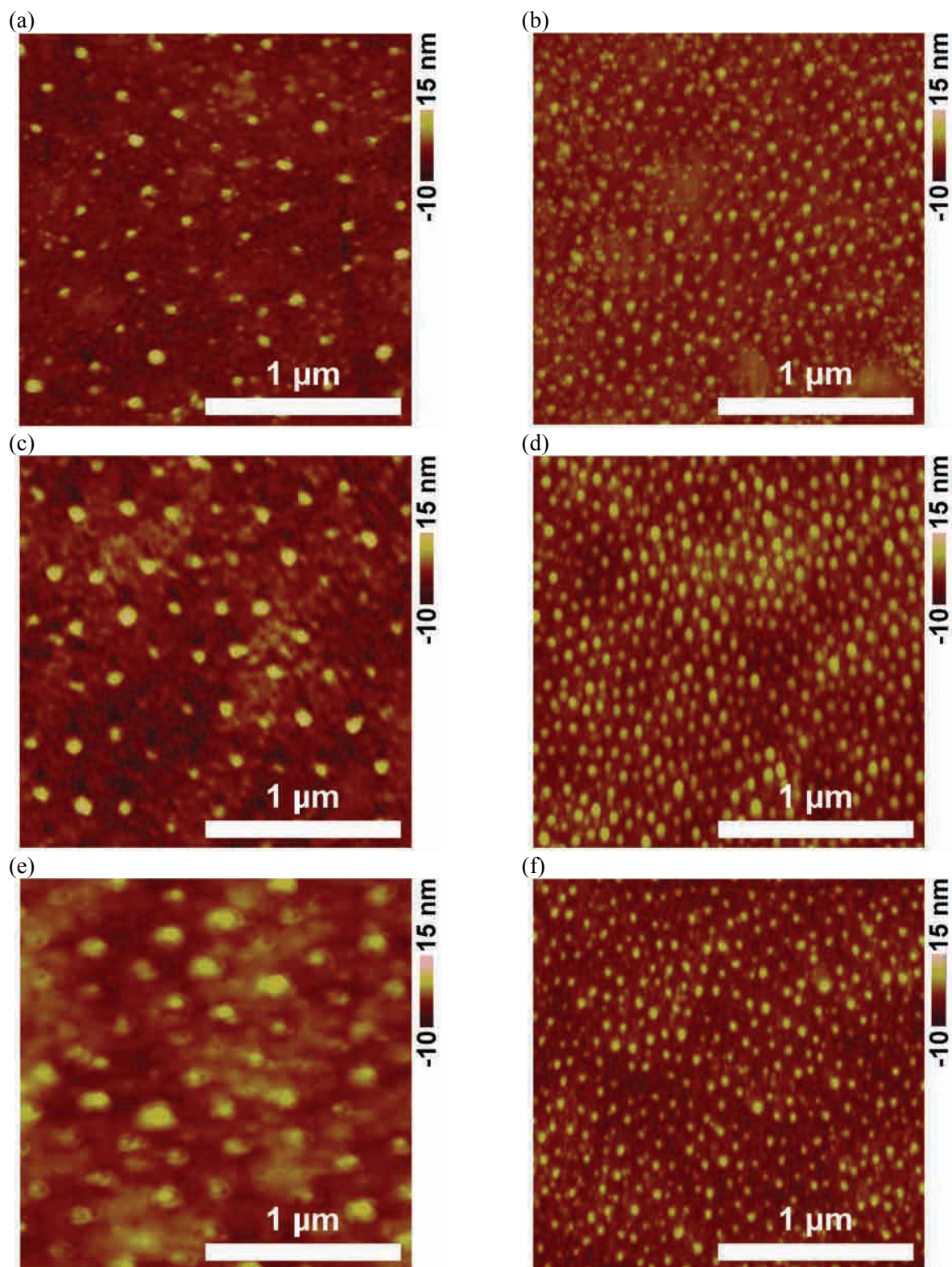
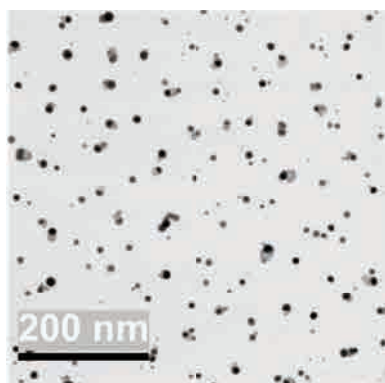
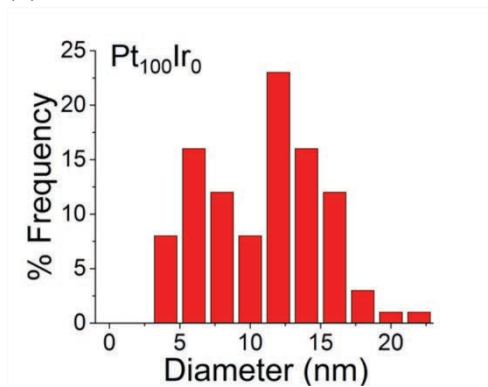


Figure S1. SFM images of arrays of $\text{Pt}_x\text{Ir}_{100-x}$ NP clusters generated from the $\text{PS}_{1392}\text{-}b\text{-P4VP}_{471}$ (a, c, e) and the $\text{PS}_{552}\text{-}b\text{-P4VP}_{174}$ (b, d, f) templates on ITO electrodes. The composition values of $\text{Pt}_x\text{Ir}_{100-x}$ NPs in these samples were determined by XPS and are: (a) $\text{Pt}_{33}\text{Ir}_{67}$, (b) $\text{Pt}_{36}\text{Ir}_{64}$, (c) $\text{Pt}_{18}\text{Ir}_{82}$, (d) $\text{Pt}_{20}\text{Ir}_{80}$, (e) $\text{Pt}_{19}\text{Ir}_{81}$, and (f) $\text{Pt}_{16}\text{Ir}_{84}$.

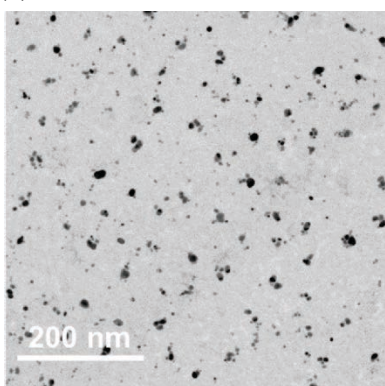
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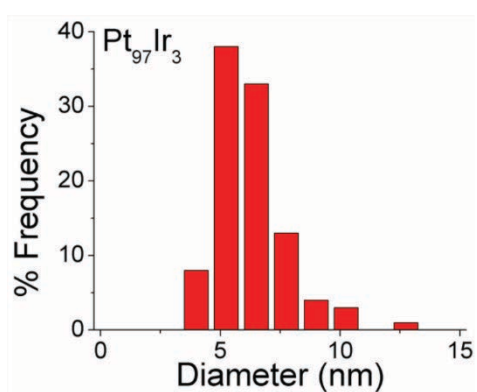
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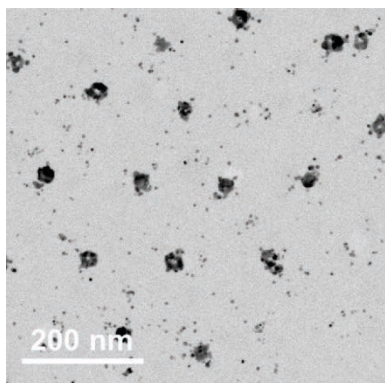
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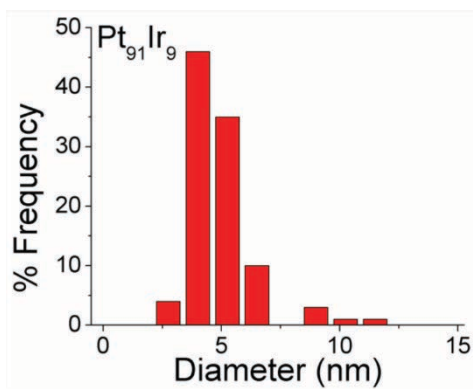
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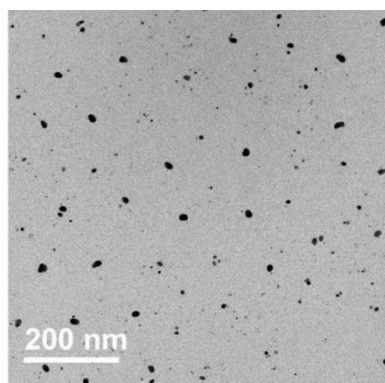
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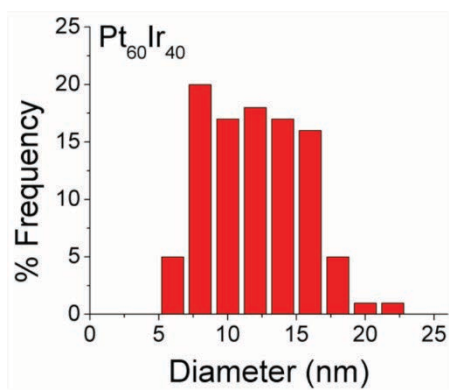
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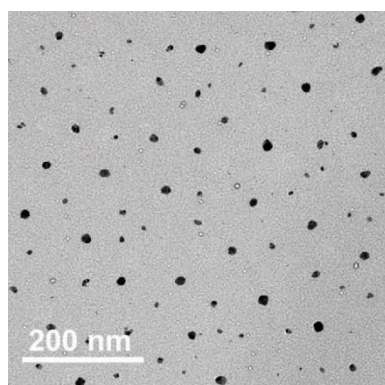
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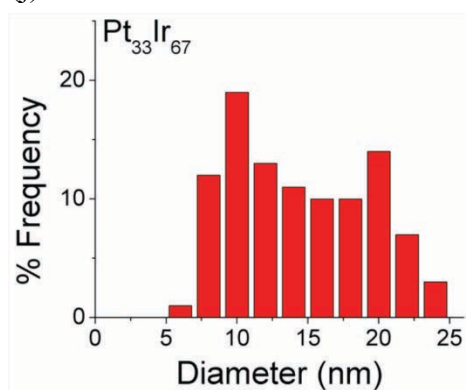
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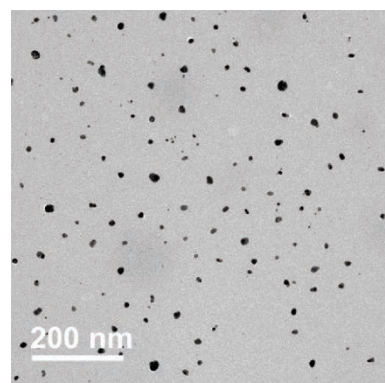
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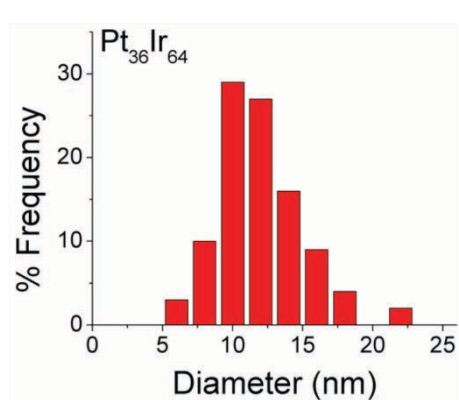
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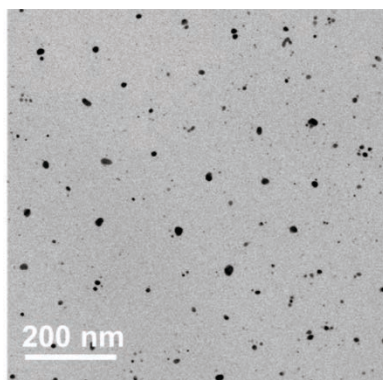
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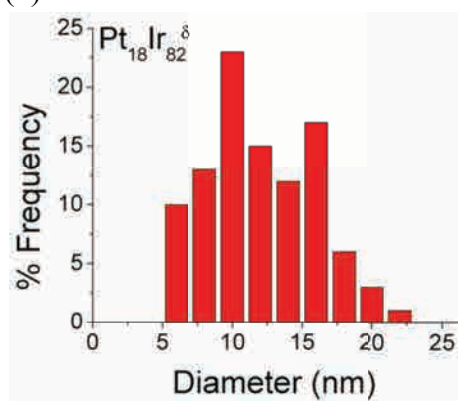
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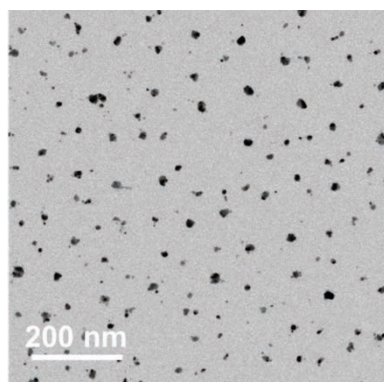
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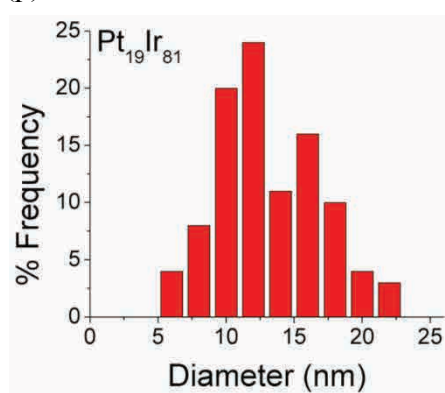
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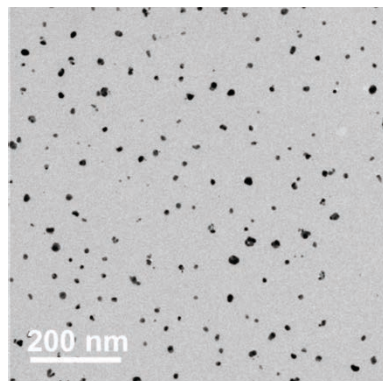
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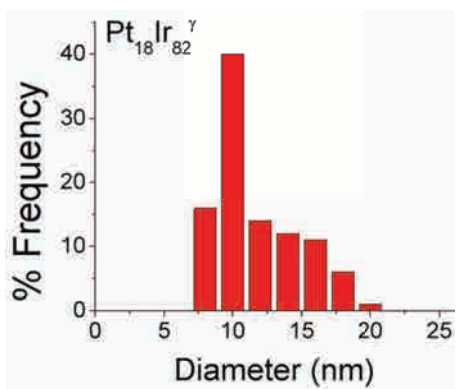
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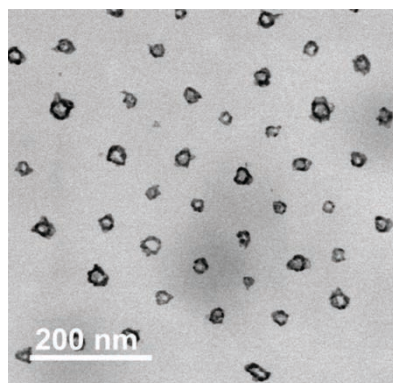
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(r)



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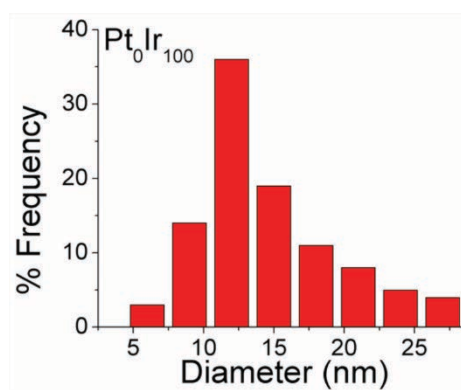
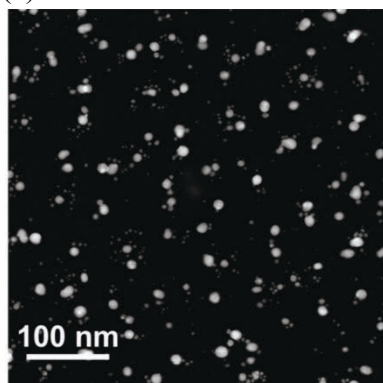
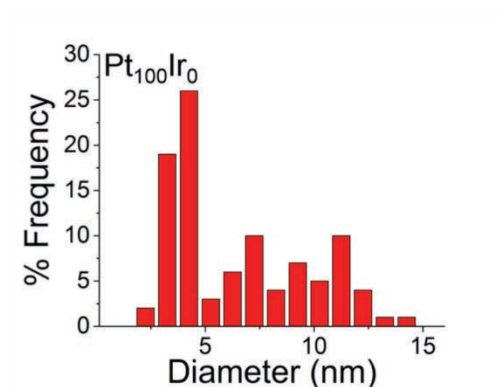


Figure S2. Bright field STEM images (left) and corresponding diameter histograms (right; avg. of 100 particles) of: (a, b) Pt₁₀₀Ir₀, (c, d) Pt₉₇Ir₃, (e, f) Pt₉₁Ir₉, (g, h) Pt₆₀Ir₄₀, (i, j) Pt₃₃Ir₆₇, (k, l) Pt₃₆Ir₆₄, (m, n) Pt₁₈Ir₈₂^δ, (o, p) Pt₁₉Ir₈₁, (q, r) Pt₁₈Ir₈₂^γ, and (s, t) Pt₀Ir₁₀₀ synthesized with the PS₁₃₉₂-*b*-P4VP₄₇₁ template.

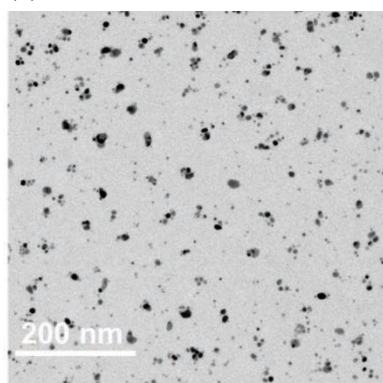
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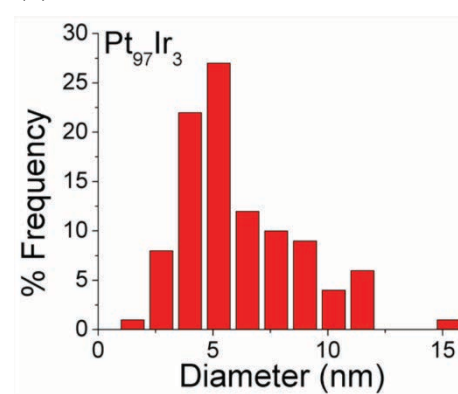
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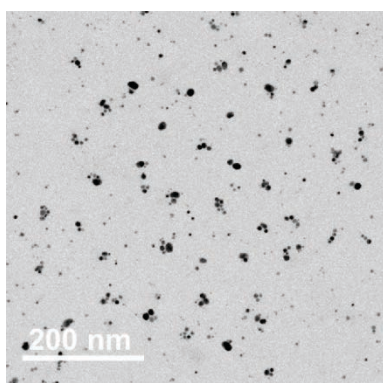
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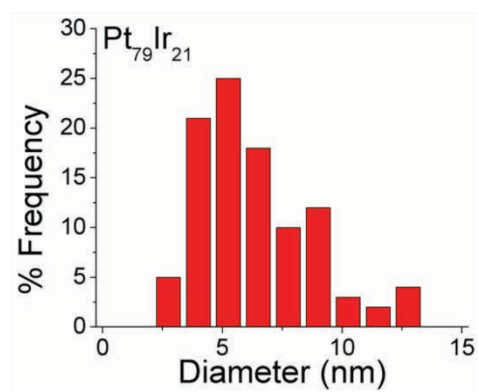
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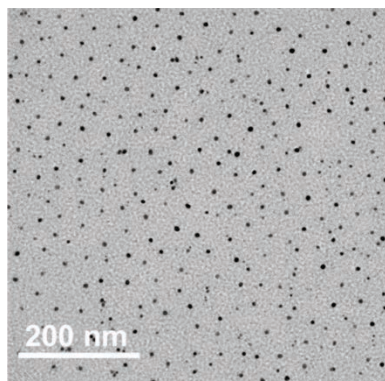
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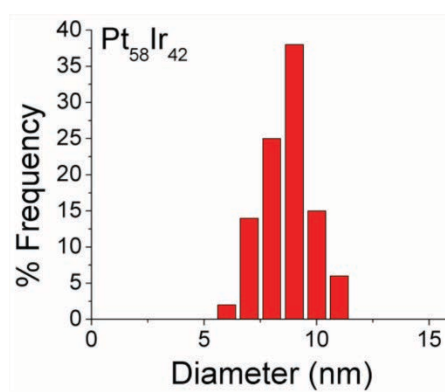
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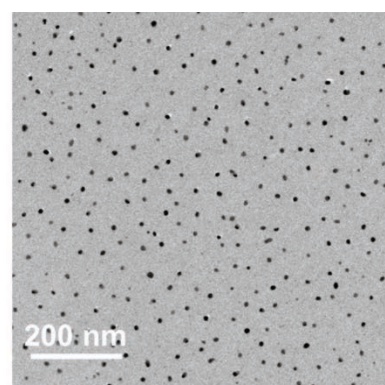
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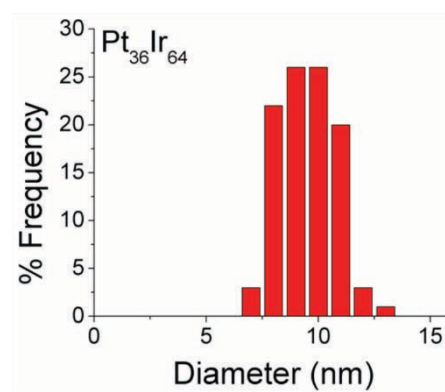
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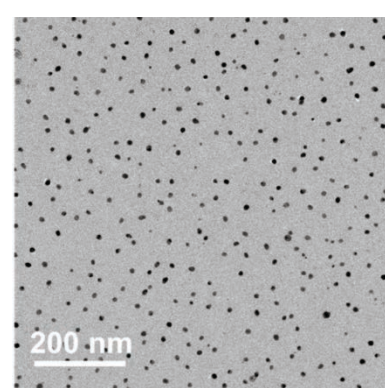
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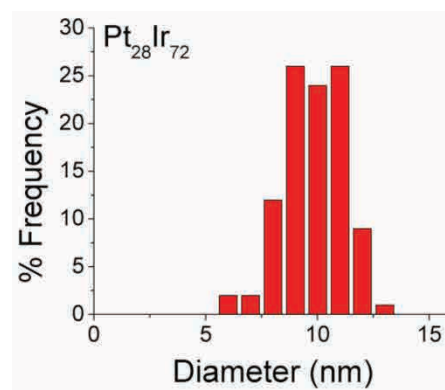
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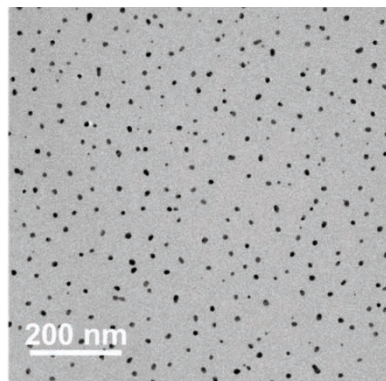
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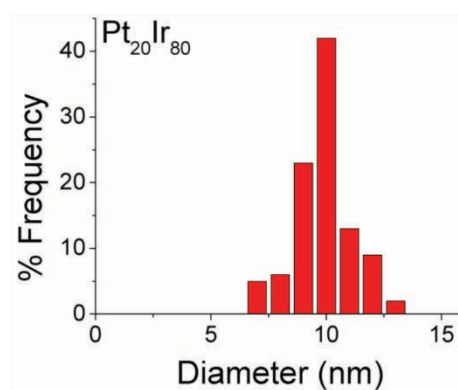
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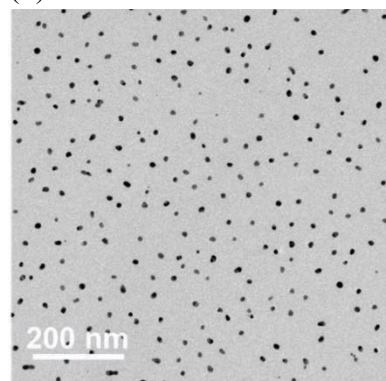
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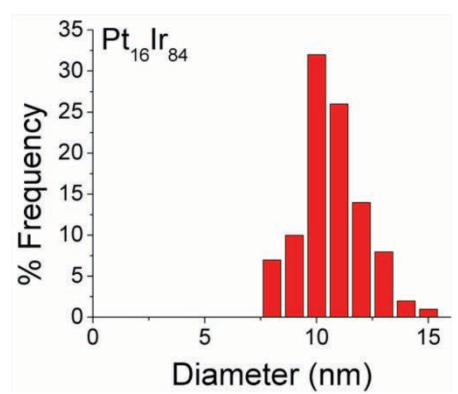
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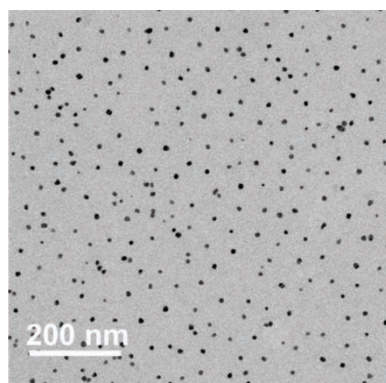
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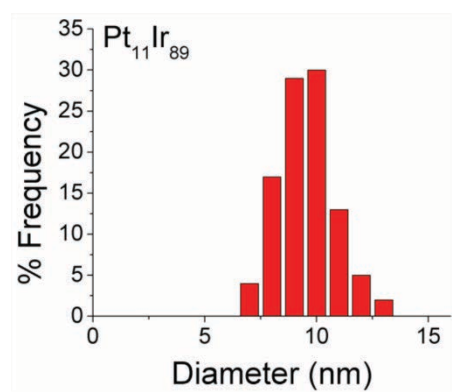
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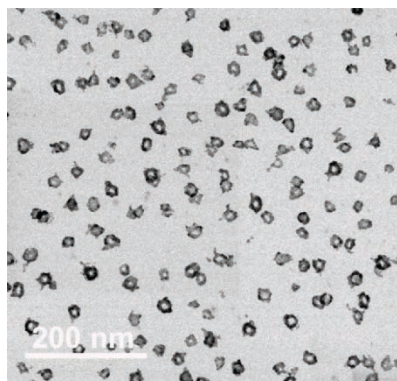
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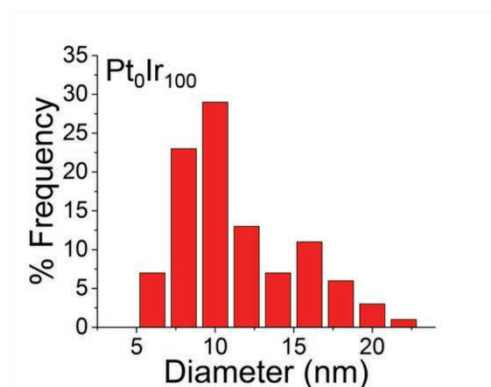
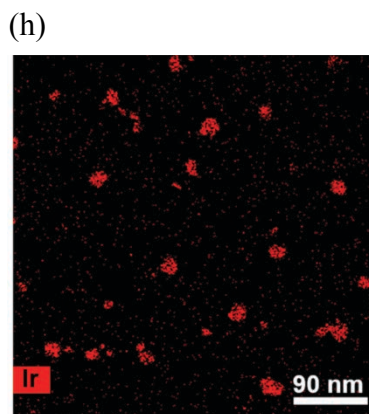
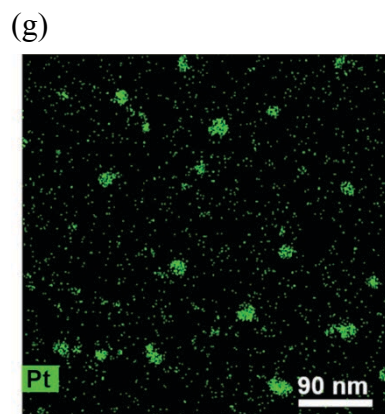
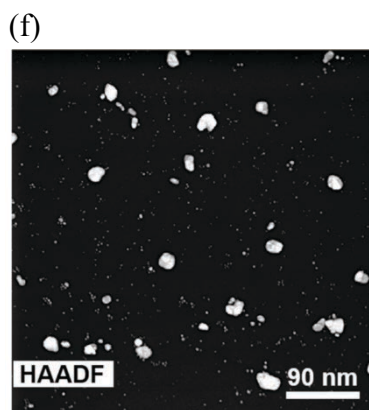
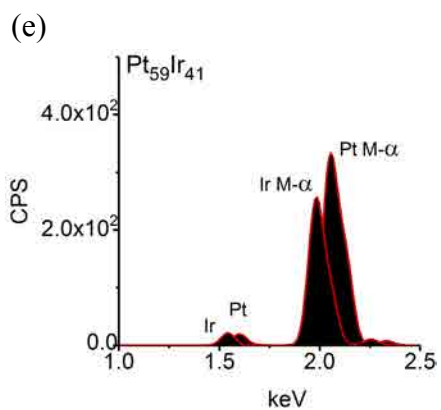
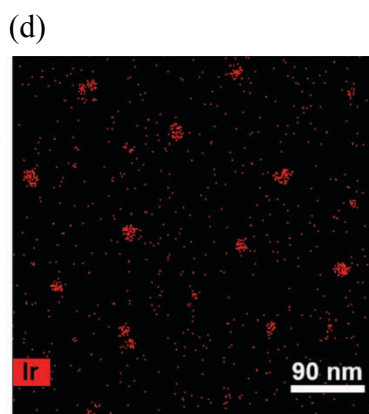
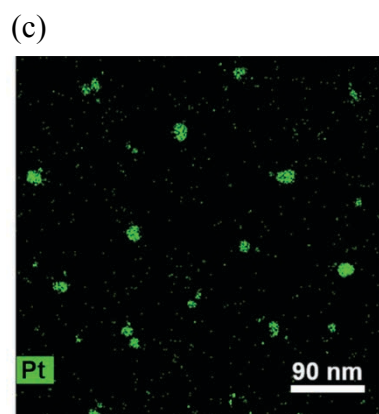
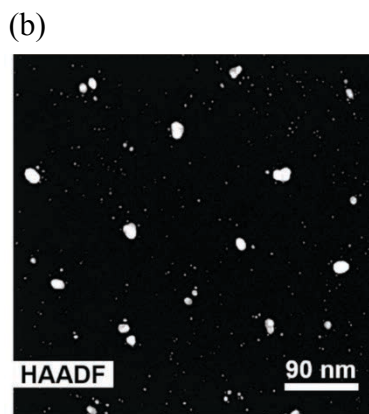
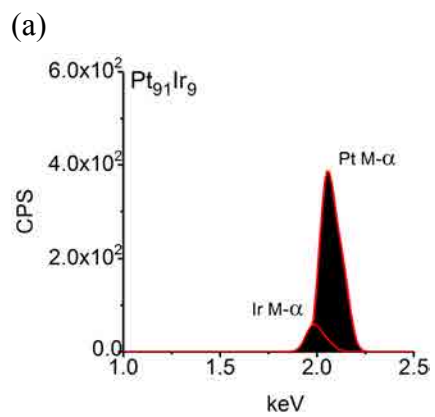
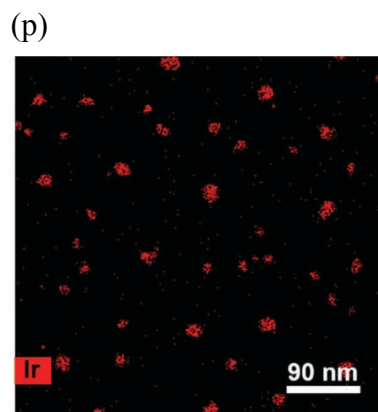
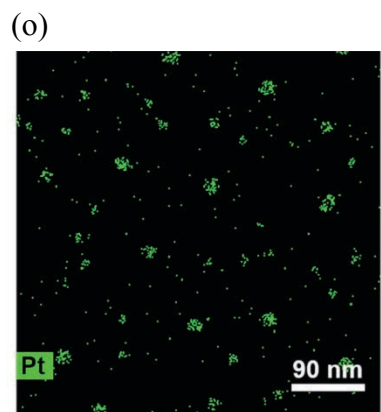
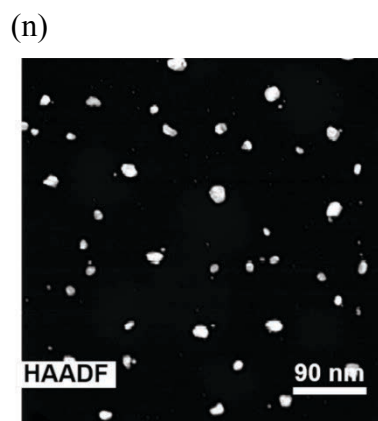
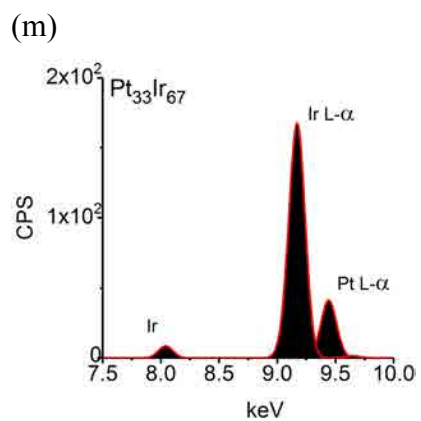
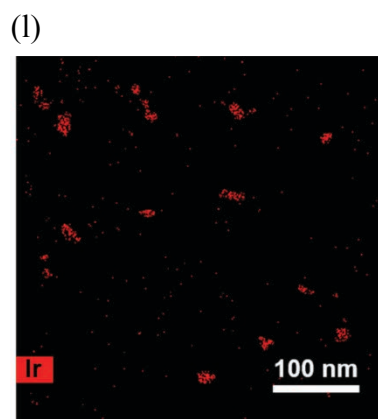
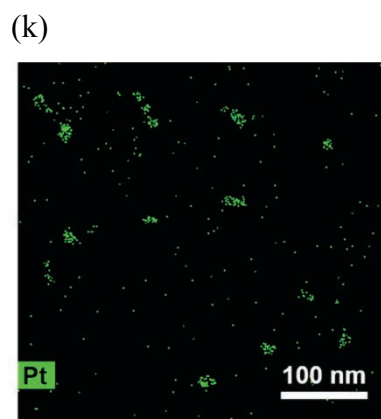
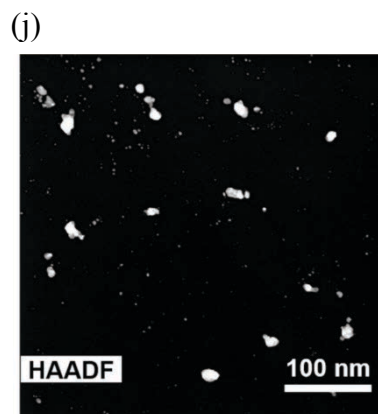
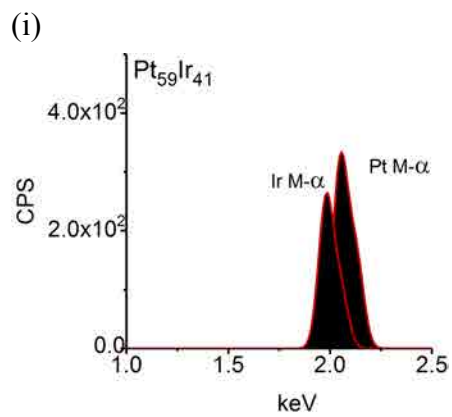
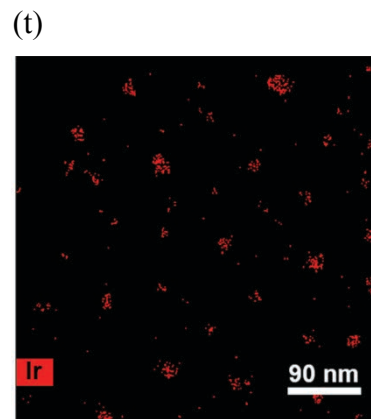
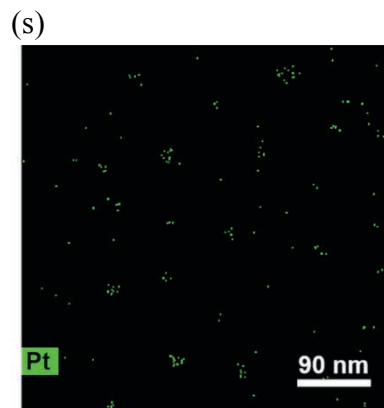
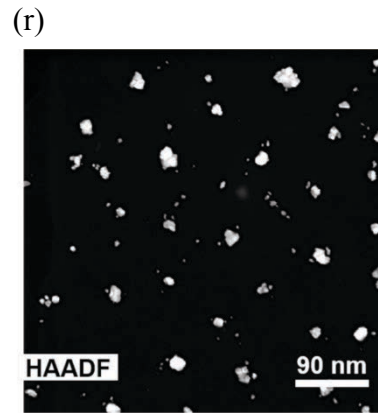
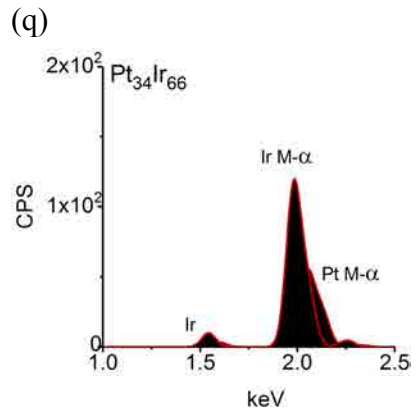


Figure S3. Bright field and HAADF STEM/TEM images (left) and corresponding diameter histograms (right; avg. of 100 particles) of: (a, b) Pt₁₀₀Ir₀, (c, d) Pt₉₇Ir₃, (e, f) Pt₇₉Ir₂₁, (g, h) Pt₅₈Ir₄₂, (i, j) Pt₃₆Ir₆₄, (k, l) Pt₂₈Ir₇₂, (m, n) Pt₂₀Ir₈₀, (o, p) Pt₁₆Ir₈₄, (q, r) Pt₁₁Ir₈₉, and (s, t) Pt₀Ir₁₀₀ synthesized with the PS₅₅₂-*b*-P4VP₁₇₄ template.







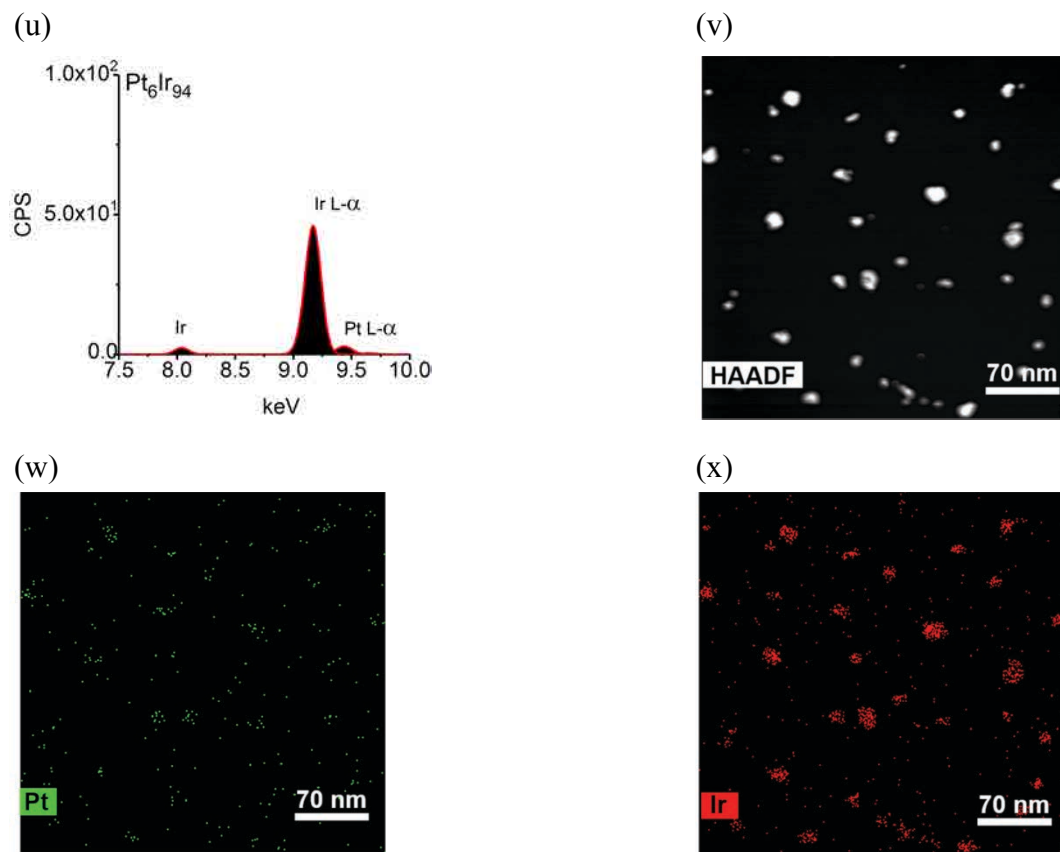
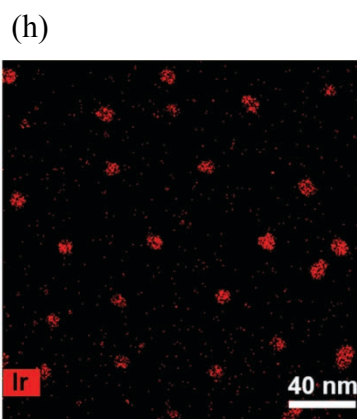
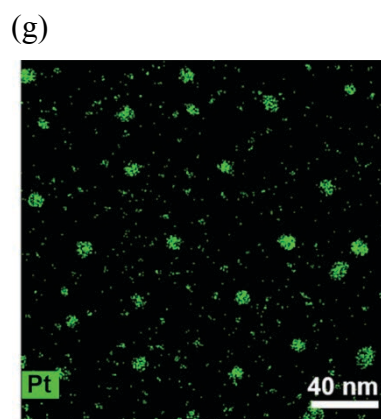
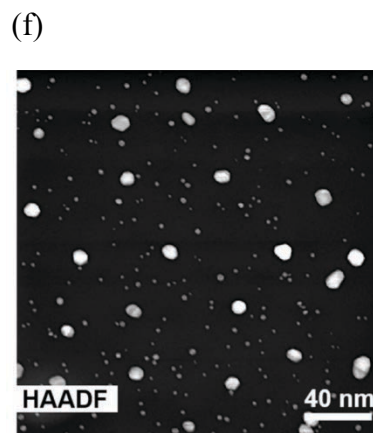
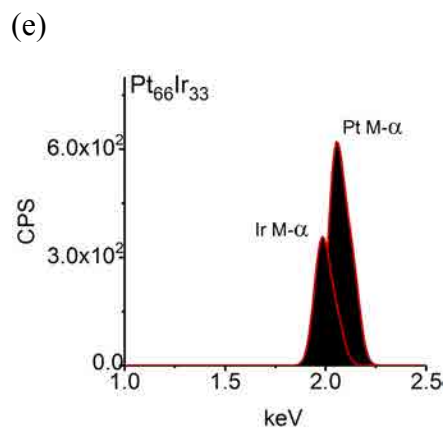
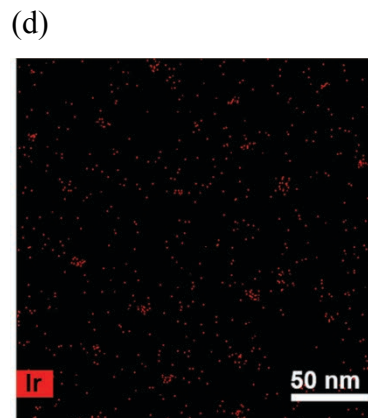
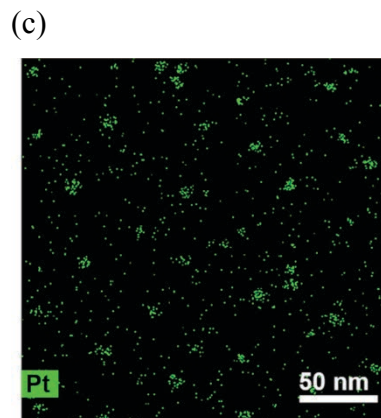
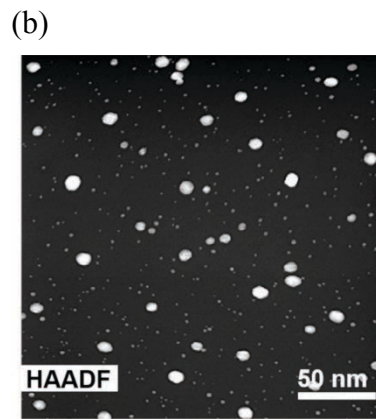
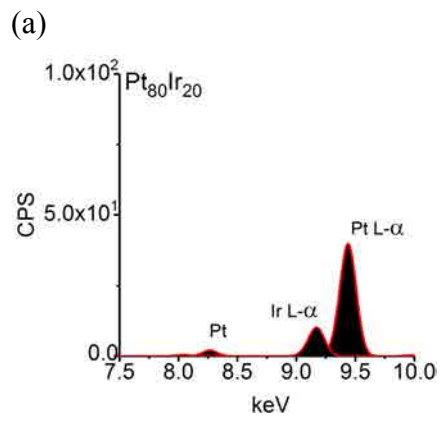
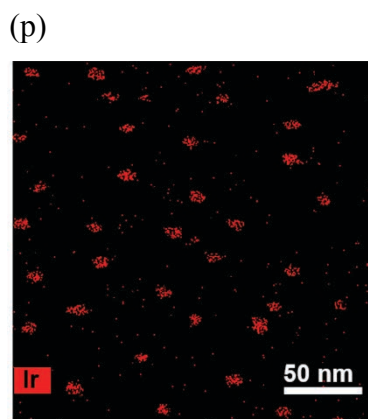
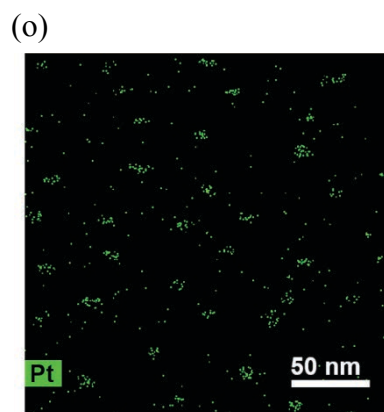
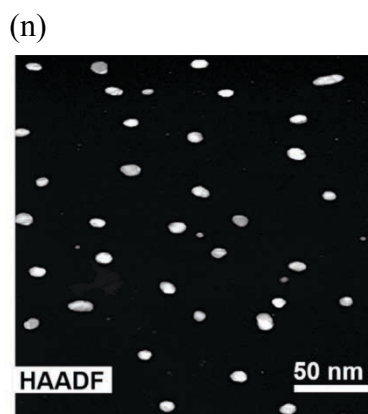
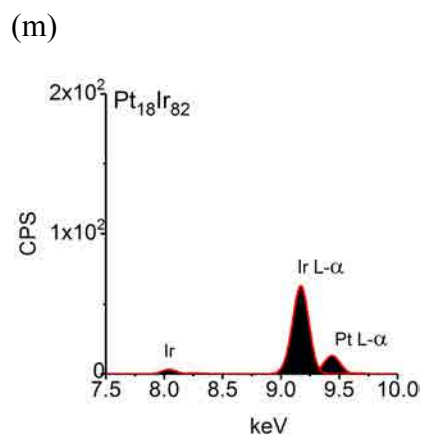
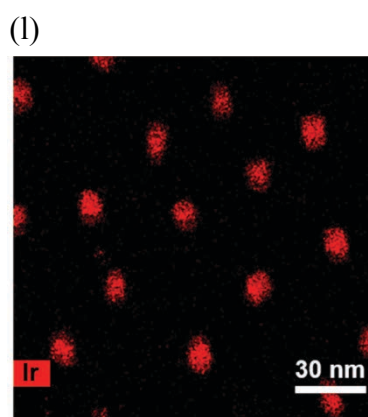
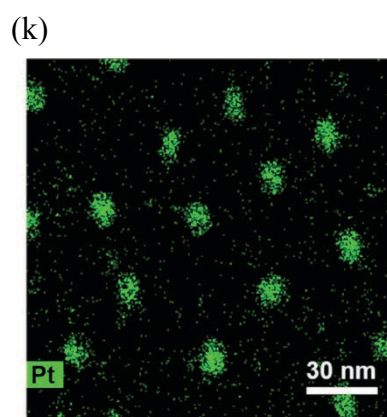
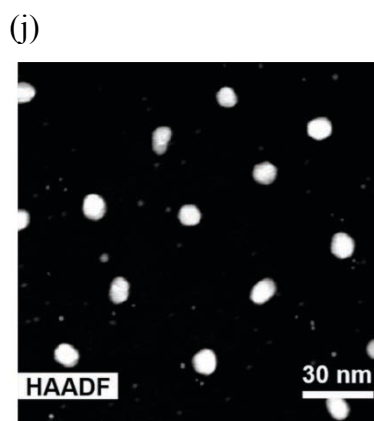
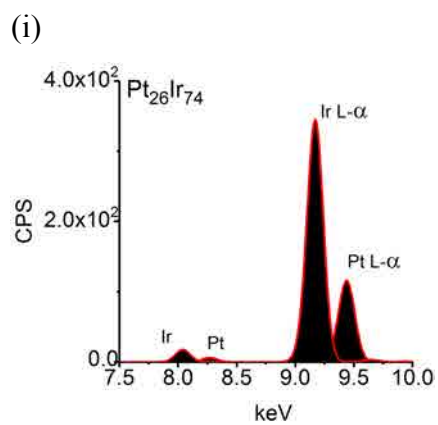
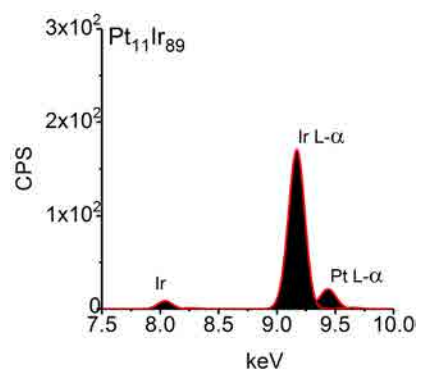


Figure S4. Bremsstrahlung corrected EDS spectra for (a, b, c, d) Pt₆₀Ir₄₀, (e, f, g, h) Pt₃₃Ir₆₇, (i, j, k, l) Pt₃₆Ir₆₄, (m, n, o, p) Pt₁₈Ir₈₂^δ, (q, r, s, t) Pt₁₉Ir₈₁, and (u, v, w, x) Pt₁₈Ir₈₂^γ NPs synthesized with the PS₁₃₉₂-*b*-P4VP₄₇₁ template. The inset labels in each graph refer to the EDS-estimated Pt:Ir ratios for 0.12 μm² areas while those in the caption refer to those determined by XPS.

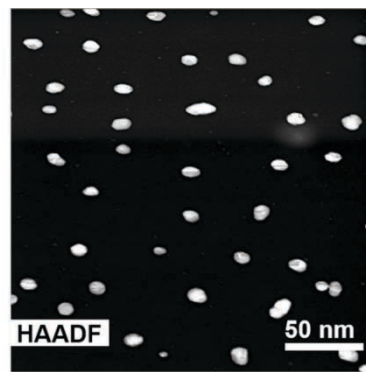




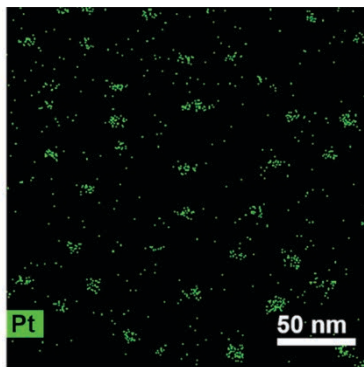
(q)



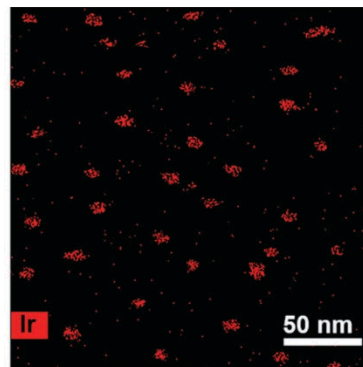
(r)



(s)



(t)



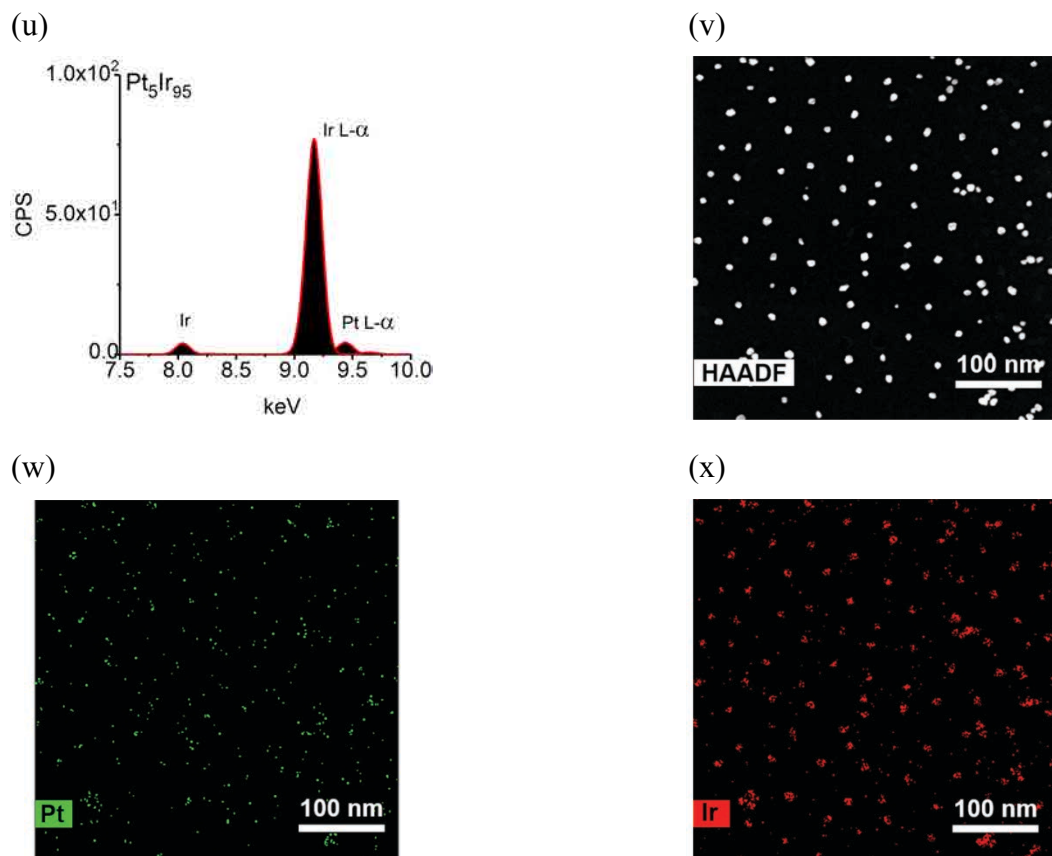


Figure S5. Bremsstrahlung corrected EDS spectra for (a, b, c, d) Pt₅₈Ir₄₂, (e, f, g, h) Pt₃₆Ir₆₄, (i, j, k, l) Pt₂₈Ir₇₂, (m, n, o, p) Pt₂₀Ir₈₀, (q, r, s, t) Pt₁₆Ir₈₄, and (u, v, w, x) Pt₁₁Ir₈₉ NPs synthesized with the PS₅₅₂-*b*-P4VP₁₇₄ template. The inset labels refer to the EDS-estimated Pt:Ir ratios for 0.056 μm^2 areas while those in the caption refer to those determined by XPS.

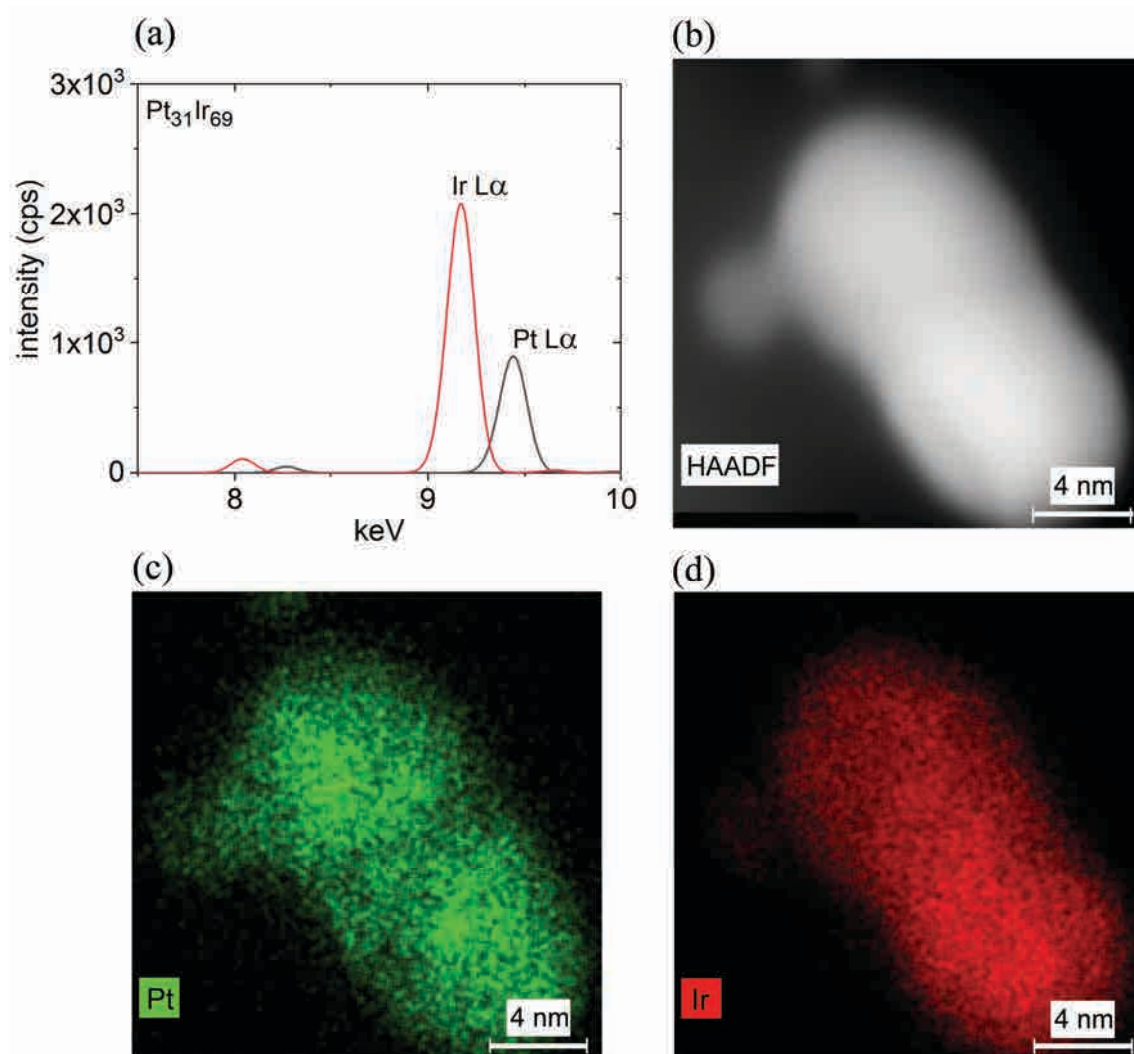


Figure S6. The Bremsstrahlung corrected high-resolution mapping of the EDS spectra for a single NP synthesized with the $\text{PS}_{552}\text{-}b\text{-P4VP}_{174}$ template from a loading bath of 8.0:2.0 with an XPS-estimated composition of $\text{Pt}_{36}\text{Ir}_{64}$. The plot in (a) shows the intensity of the $L\alpha$ emission obtained from the NP shown in the (b) HAADF image. The (c) Pt elemental map and the (d) Ir elemental map are also shown. The inset in (a) is the EDS-estimated composition of the particle.

Shown in Figure S6 and S7 are the HR-TEM images for individual NPs isolated from arrays of clusters of PtIr NPs created from the PS₁₃₉₂-*b*-P4VP₄₇₁ and PS₅₅₂-*b*-P4VP₁₇₄ templates, respectively. Each image in S6 and S7 shows a crystalline NP with resolved lattice planes for loading baths of 8.0:2.0, 7.5:2.5, and 2.4:7.6 (a-c), respectively. This observation is more clearly identified by the Fast-Fourier Transform (FFT) of these images, which are presented as insets. These FFT-images reveal pronounced intensities at the reciprocal radii positions labelled by Miller indices in the associated figures. The highlighted intensities in the FFT of the TEM image in Figure S6 a-c correspond to {111}, {111} and {200} lattice planes with unit cell distances of 3.90, 3.85 and 3.81 Å, respectively. Figure S7 a-c show individual particles with FFT insets that correspond to unit cell distances of 3.87, 3.86, and 3.83 Å for lattice planes of {111}. The average lattice constants for Pt and Ir are 3.92 and 3.84 Å, respectively.^{S11-S12} The unit cell dimensions are, therefore, in close agreement with bulk solid solutions of Pt and Ir^{S13-S16} and further validate alloy structure inferred from STEM-EDS data.

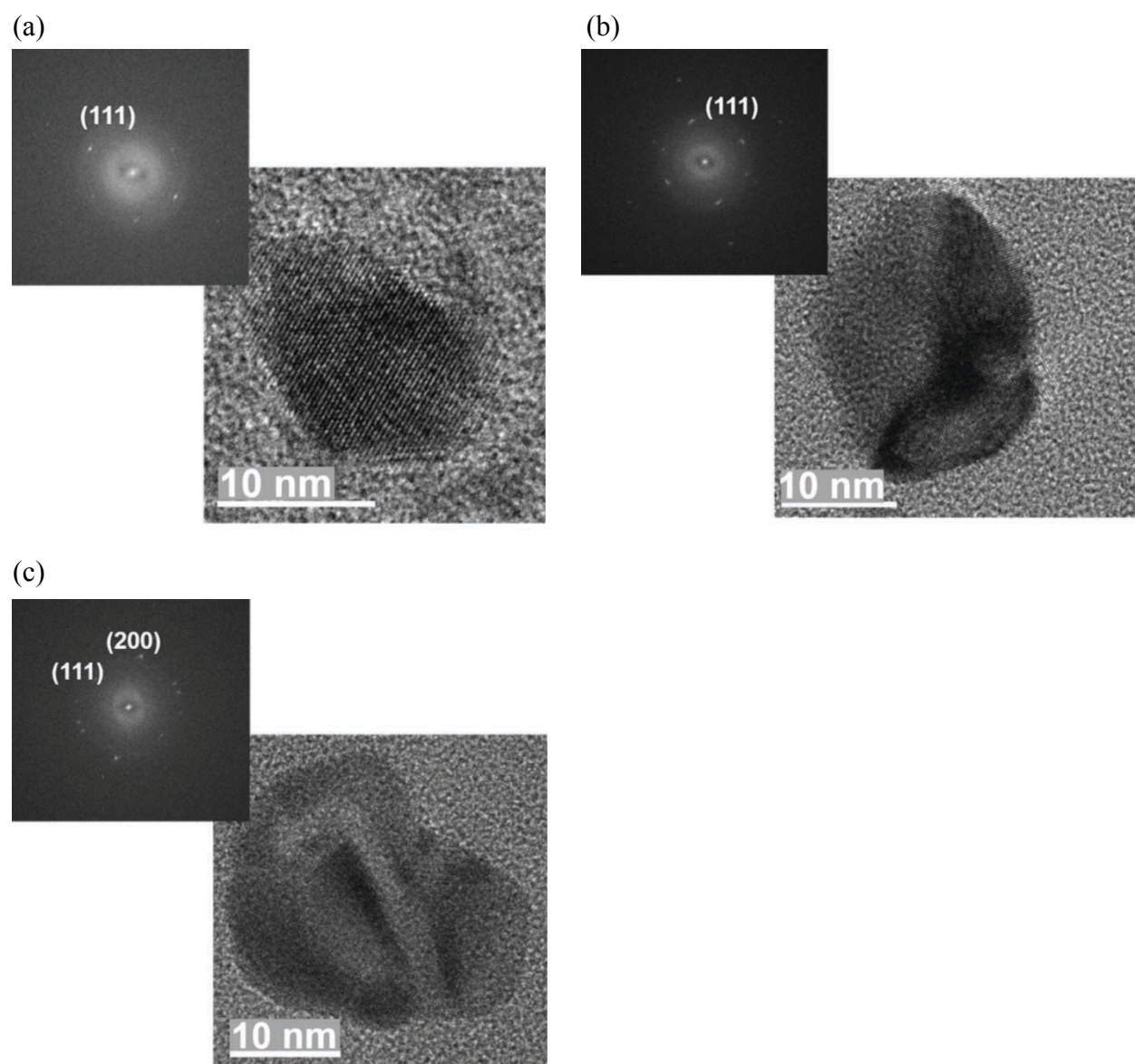


Figure S7. HR-TEM images of single PtIr NPs for (a) Pt₃₃Ir₆₇, (b) Pt₃₆Ir₆₄, and (c) Pt₁₈Ir₈₂^γ synthesized from the PS₁₃₉₂-*b*-P4VP₄₇₁ template. The insets are the corresponding Fast-Fourier

Transform (FFT) images with the labeled assignments included for the lattice planes observed in the HR-TEM images.

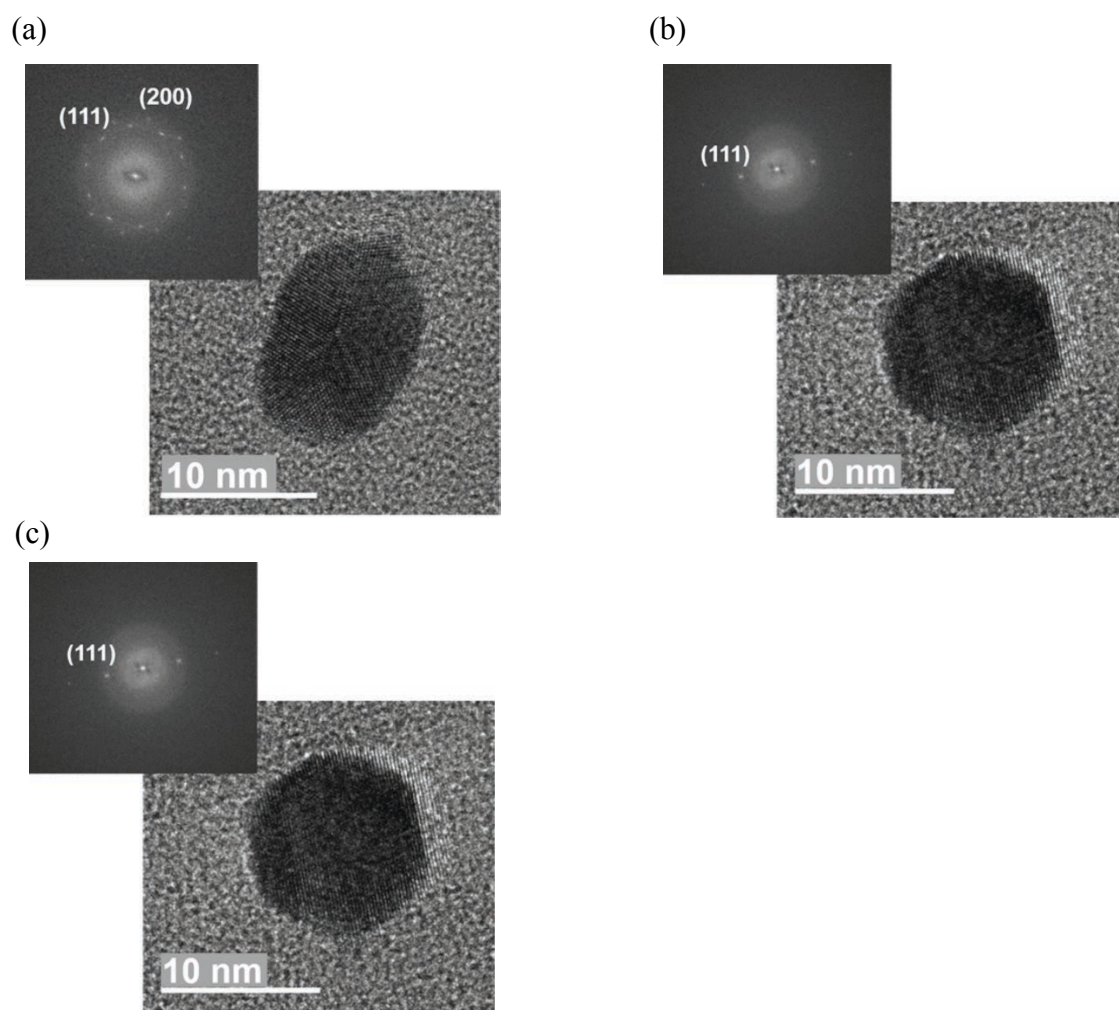


Figure S8. HR-TEM images of single PtIr NPs for (a) Pt₃₆Ir₆₄, (b) Pt₂₈Ir₇₂, and (c) Pt₁₁Ir₈₉, synthesized from the PS₅₅₂-*b*-P4VP₁₇₄ template. The insets are the corresponding FFT images with the labeled assignments included for the lattice planes observed in the HR-TEM images.

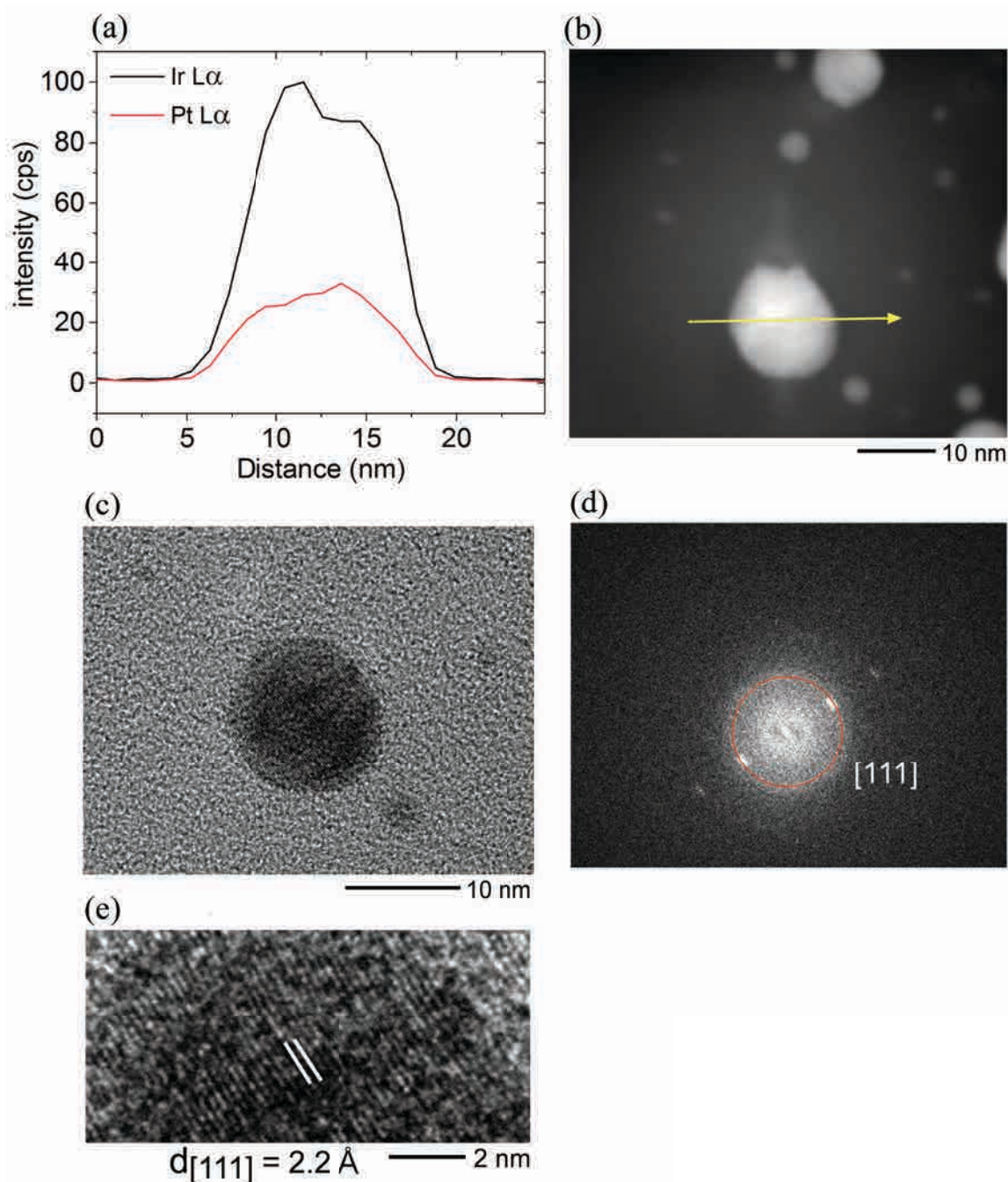


Figure S9. Representative (a) EDS line-scan profile of a single NP synthesized from the PS₅₅₂-*b*-P4VP₁₇₄ template from a Pt:Ir loading bath of 8.0:2.0. The corresponding (b) HAADF is shown and the yellow line indicates the direction of the line profile. The matching (c) HR-TEM image and (d) FFT image with the labeled assignment indicate a {111} lattice plane. In (e) the lattice fringe pattern suggests a d-spacing of 2.2 Å, which matches the calculated d-spacing from the FFT image in (d). The calculated d-spacing of 2.2 Å is in agreement with the {111} plane d-spacing for a Pt₁₇Ir₈₃ composition determined by XRD (JCPDS No. 01-088-1728).

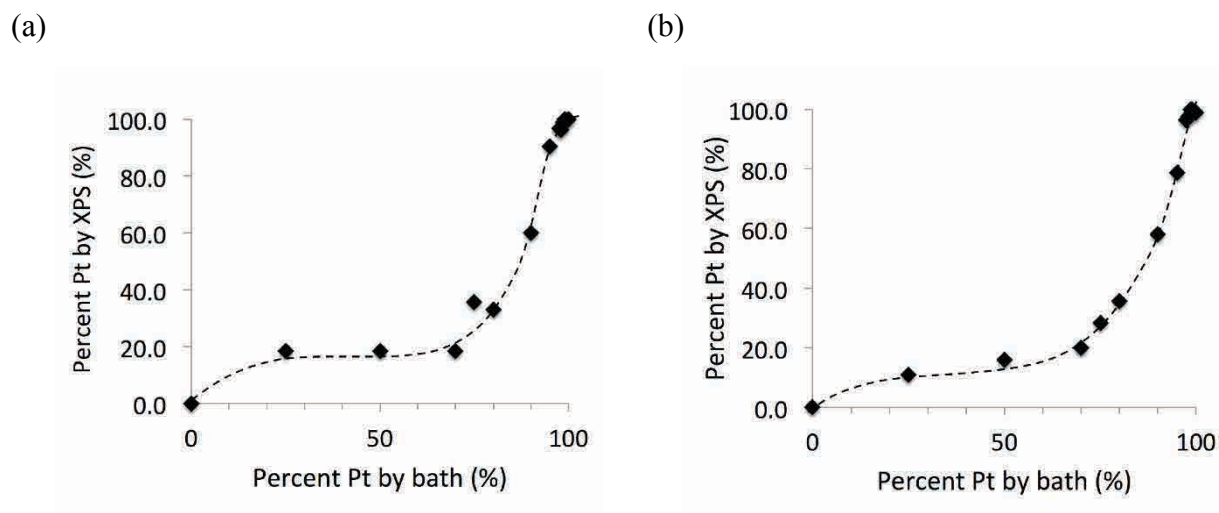


Figure S10. The ICP-MS- and XPS-estimated mass loadings of Pt for the $\text{Pt}_x\text{Ir}_{100-x}$ NPs synthesized from (a) $\text{PS}_{1392}\text{-}b\text{-P4VP}_{471}$ and (b) $\text{PS}_{552}\text{-}b\text{-P4VP}_{174}$ templates.

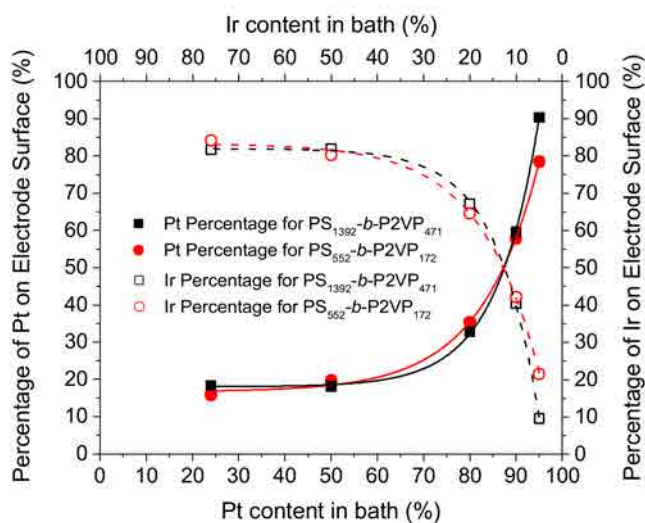


Figure S11. The ICP-MS- and XPS-estimated percentages of Pt (solid symbols) and Ir (open symbols) on the electrode surface for selected bimetallic $\text{Pt}_x\text{Ir}_{100-x}$ NPs synthesized from $\text{PS}_{1392}\text{-}b\text{-P4VP}_{471}$ (square symbols) and $\text{PS}_{552}\text{-}b\text{-P4VP}_{174}$ (circle symbols) templates.

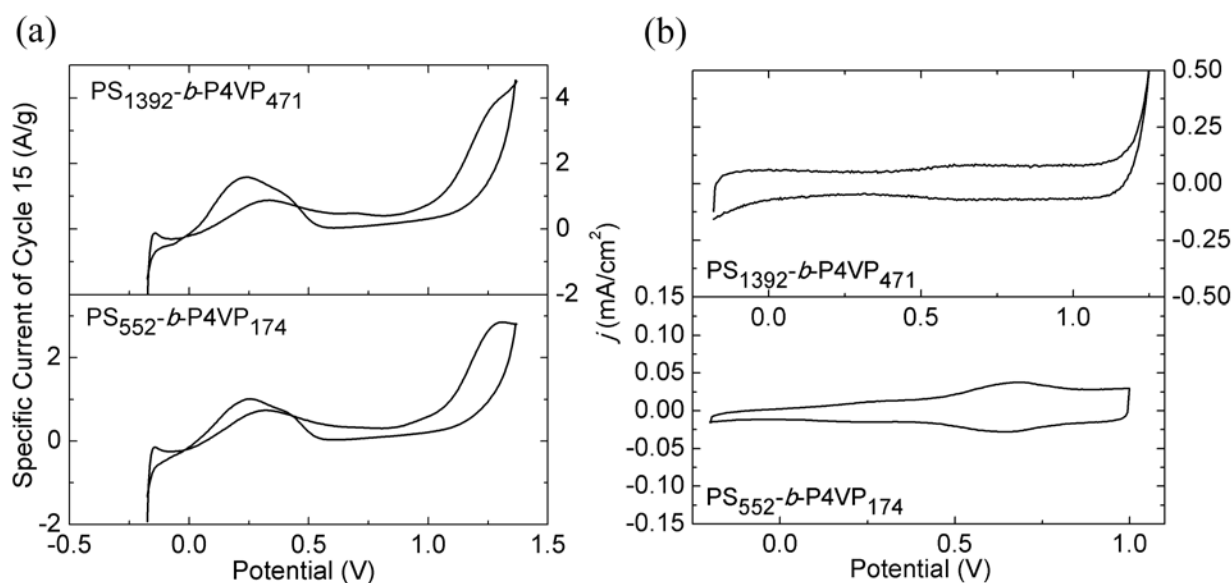


Figure S12. Formic acid oxidation plots for the monometallic NP arrays supported on ITO. The (a) 15th CV cycle of the Pt analogues showing the specific current (normalized for mass loading) and the (b) 2nd CV cycle of the monometallic Ir NP arrays reported in current density, which was determined from the geometric area of the electrode. The CV data was acquired in 100 mM HCOOH and 100 mM H₂SO₄. The notation shown in each of the plots indicates the type of block copolymer used to prepare the NP catalyst arrays. The oxidation of formic acid on Ir NPs does not exhibit any of the characteristics for monometallic Pt or bimetallic Pt_{*x*}Ir_{100-*x*} NPs. The cycle 15 *I*_{1a} and *I*₃ values for monometallic Pt NPs produced from PS₁₃₉₂-*b*-P4VP₄₇₁ were 2.66 A/g and 4.56 A/g, respectively, while those for the PS₅₅₂-*b*-P4VP₁₇₄ were 1.14 A/g and 1.60 A/g, respectively.

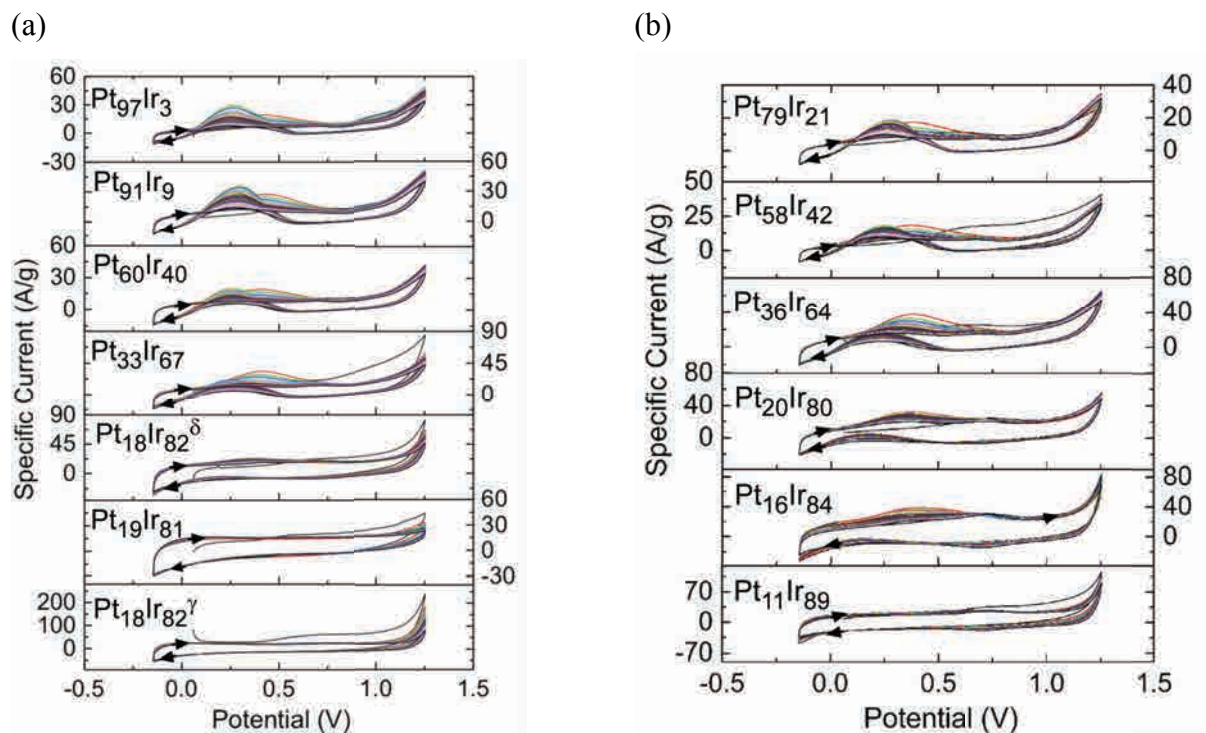


Figure S13. Shown are the 25-cycle CV plots (100 mM H_2SO_4 and 100 mM HCOOH , 10 mV/s) for ITO-supported $\text{Pt}_x\text{Ir}_{100-x}$ NPs synthesized from the (a) $\text{PS}_{1392}\text{-}b\text{-P4VP}_{471}$ and (b) $\text{PS}_{552}\text{-}b\text{-P4VP}_{174}$ templates. The inset labels refer to the XPS-estimated Pt:Ir ratio of the NP clusters. The arrows indicate the direction of the CV scans.

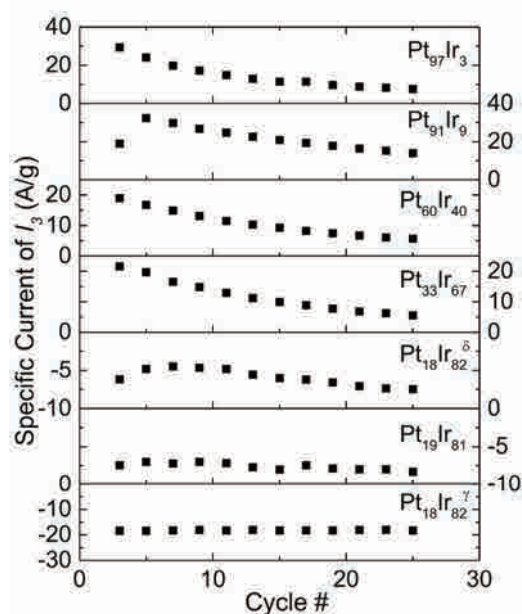


Figure S14. Mass specific current for I_3 versus cycle number for PtIr NP arrays synthesized from $\text{PS}_{1392}\text{-}b\text{-P4VP}_{471}$. All PtIr NP arrays are supported on ITO. The CV data was acquired in 100 mM HCOOH and 100 mM H_2SO_4 with a potential scan rate of 10 mV/s. The subscripts in the inset $\text{Pt}_x\text{Ir}_{100-x}$ labels denote the XPS-estimated compositions.

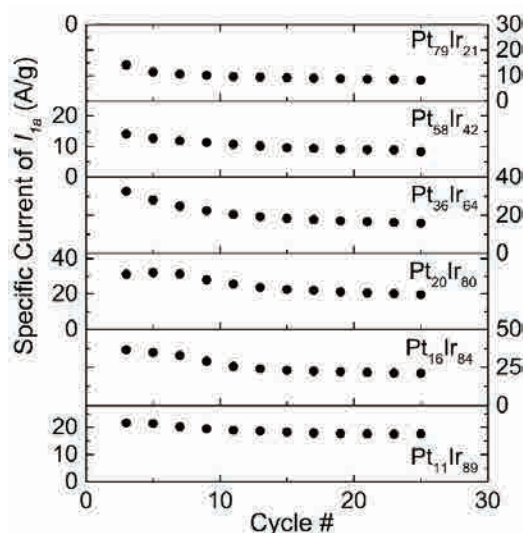


Figure S15. Mass specific current for I_3 versus cycle number for PtIr NP arrays synthesized from PS₅₅₂-*b*-P4VP₁₇₄. All PtIr NP arrays are supported on ITO. The CV data was acquired in 100 mM HCOOH and 100 mM H₂SO₄ with a potential scan rate of 10 mV/s. The subscripts in the inset Pt_xIr_{100-x} labels denote the XPS-estimated composition.

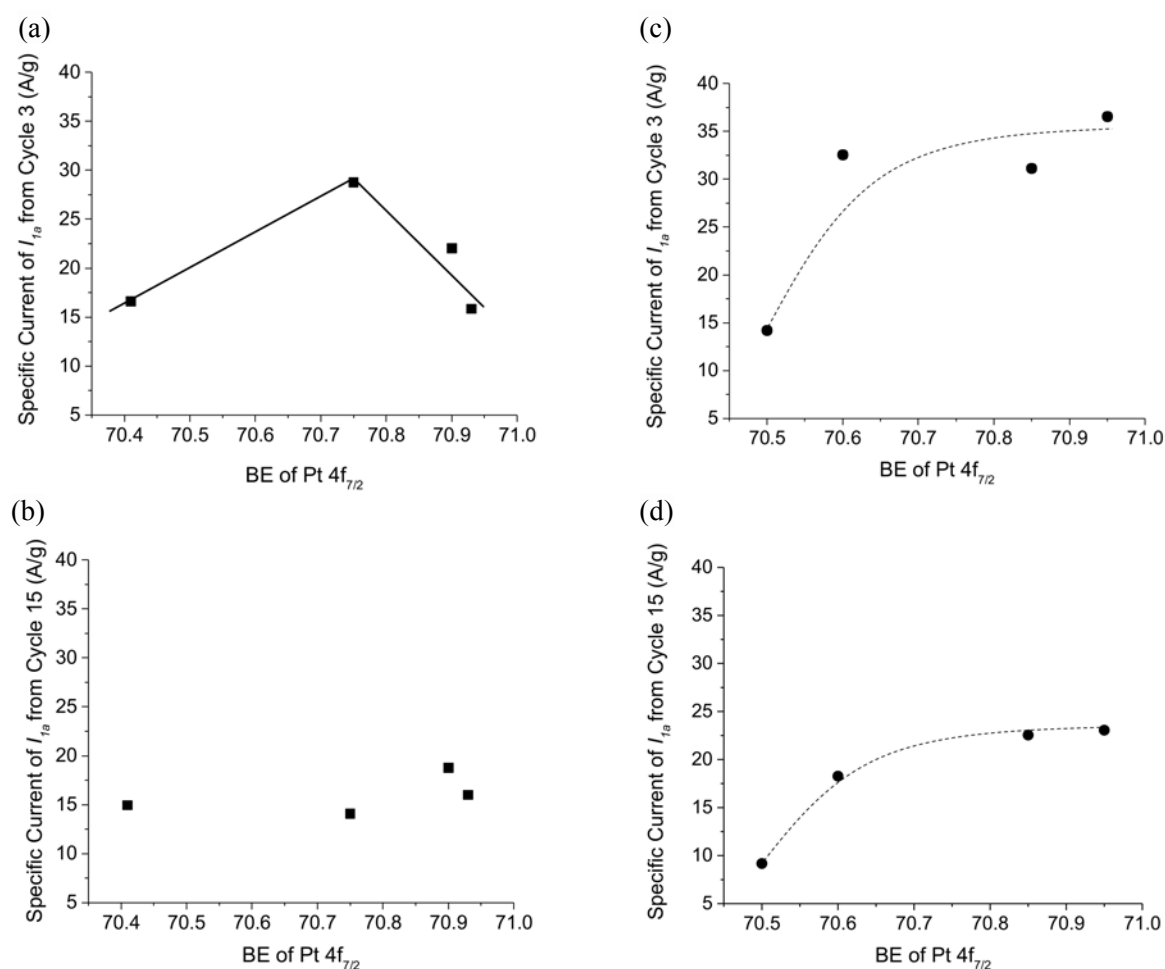


Figure S16. Plot for I_{3a} peak current of Pt_xIr_{100-x} NPs synthesized from PS₁₃₉₂-*b*-P4VP₄₇₁ (square symbols) and PS₅₅₂-*b*-P4VP₁₇₄ (circle symbols) versus the binding energy for the respective Pt 4f_{7/2} peak found by XPS. Data in (a) and (c) were obtained from cycle 3 of a 25 cycle study while data in (b) and (d) were obtained from cycle 15 of a 25 cycle study.

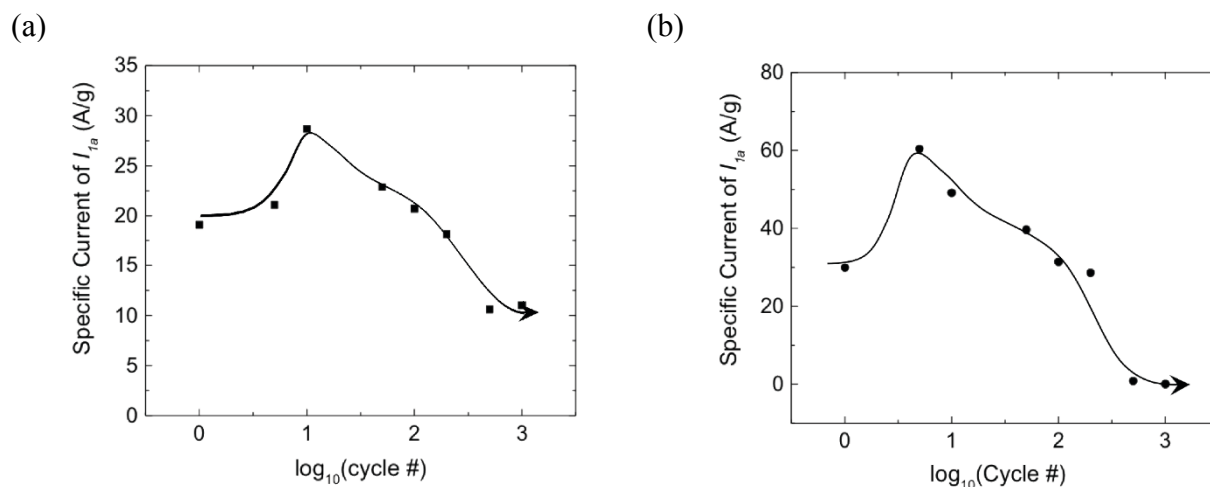


Figure S17. Mass specific current for the formic acid oxidation reaction versus log of cycle number for a multi-cycle study for (a) Pt₁₈Ir₈₂ NPs synthesized from PS₁₃₉₂-*b*-P4VP₄₇₁ and (b) Pt₂₀Ir₈₀ NPs synthesized from PS₅₅₂-*b*-P4VP₁₇₄ templates. The trend lines are intended to guide the eye.

References:

- (S1) C. Xu; Q. Hao; H. Duan, *J. Mater. Chem A* 2014, **2** (23), 8875-8880.
 (S2) S. Hu; L. Scudiero; S. Ha, *Electrochem. Commun.* 2017, **38**, 107-109.
 (S3) M. Scofield; C. Koenigsmann; L. Wang; H. Liu; S. S. Wong, *Energy Environ. Sci.* 2015, **8** (1), 350-363.
 (S4) S. Hu; F. Munoz; J. Noborikawa; J. Haan; L. Scudiero; S. Ha, *Appl. Catal. B.* 2016, **180**, 758-765.
 (S5) W. Chen; J. Kim; S. Sun; S. Chen, *Langmuir* 2007, **23** (22), 11303-11310.
 (S6) O. Winjobi; Z. Zhang; C. Liang; W. Li, *Electrochim. Acta* 2010, **55** (13), 4217-4221.
 (S7) R. Wang; C. Wang; W. B. Cai; Y. Ding, *Adv. Mater.* 2010, **22** (16), 1845-1848.
 (S8) J. Shim; J. Lee; Y. Ye; J. Hwang; S. K. Kim; T. H. Lim; U. Wiesner; J. Lee, *ACS Nano* 2012, **6** (8), 6870-6881.
 (S9) W. Chen; J. Kim; L. P. Xu; S. Sun; S. Chen, *J. Phys. Chem. C* 2007, **111** (36), 13452-13459.
 (S10) Y. Z. Lu; W. Chen, *Chem. Commun.* 2011, **47** (9) 2541-2543.
 (S11) J. B. Xu; T. S. Zhao; W. W. Yang; S. Y. Shen, *Int. J. Hydrogen Energy.* 2010, **35** (16), 8699-8706.
 (S12) J. Y. Chen; T. Herricks; M. Geissler; Y. N. Xia, *J. Am. Chem. Soc.* 2004, **126** (35), 10854-10855.
 (S13) E. Irissou; F. Laplante; S. Garbarino; M. Chaker; D. Guay, *J. Phys. Chem. C* 2010, **114** (5), 2192-2199.
 (S14) H. Okamoto; T. B. Massalski, *J. Phase Equilib.* 1985, **6** (1), 46-56.
 (S15) A. Suzuki; M. Harada; Y. N. Wu; H. Murakami, *Mater. Trans.* 2005, **46** (8), 1760-1763.
 (S16) R. E. Bedford; G. Bonnier; H. Mass; F. Pavese, *Metrologia* 1996, **33** (2), 133.