Electronic supplementary information (ESI)

Molecular cluster route for a facile synthesis of stable and active Pt nanoparticle catalyst

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Figure S1. ILTEM setup for the electrochemical test and the location of the 5 macro-region of interest across the TEM grid.

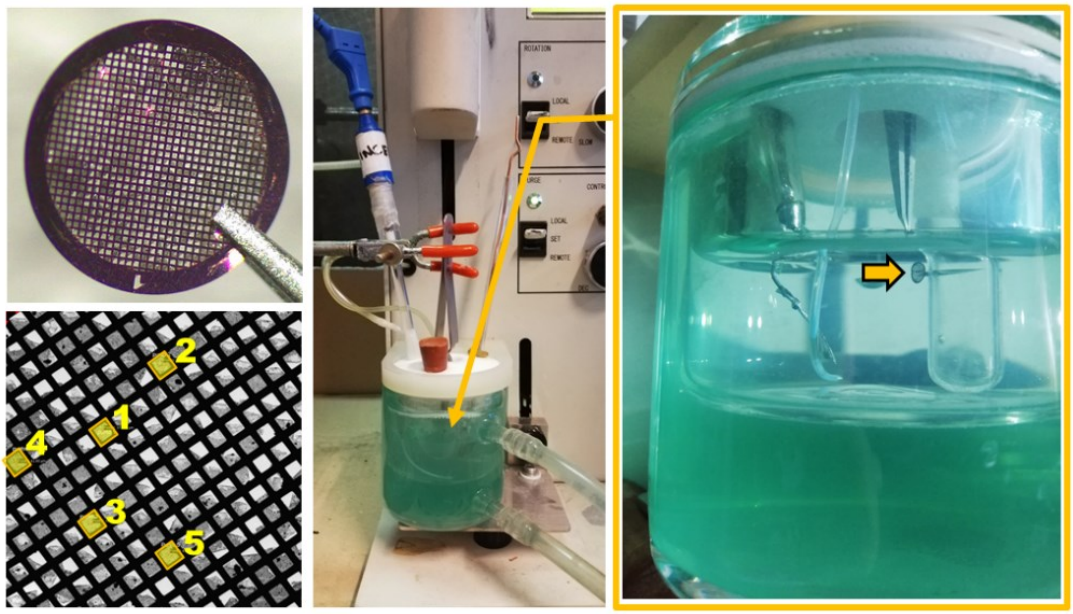

Figure S2. STEM overview of the Pt24 sample. Pt NPs appear brighter with respect to the carbon support.

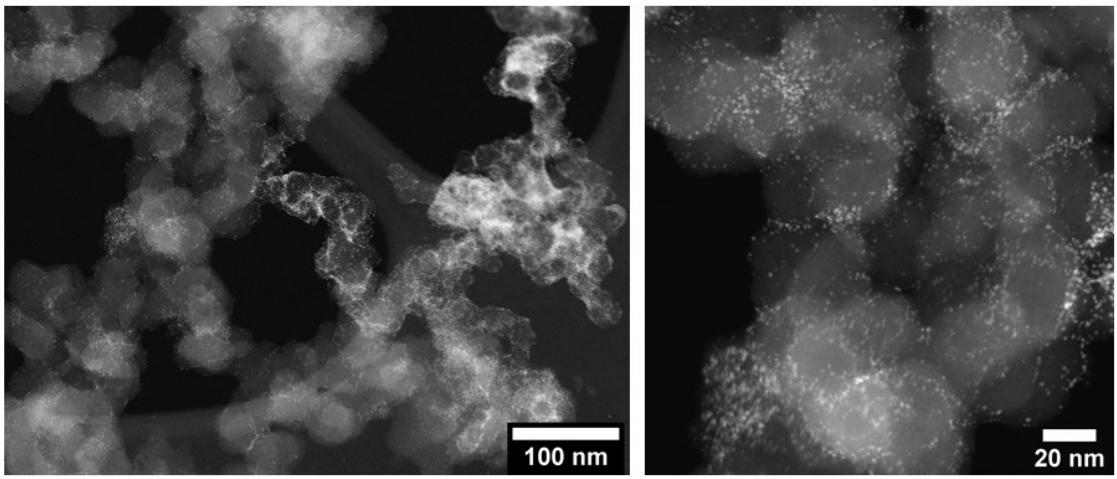

Figure S3. Cumulative frequency for NPs size distribution of the sample Pt24 across ILTEM analysis at t0, t1 and t6

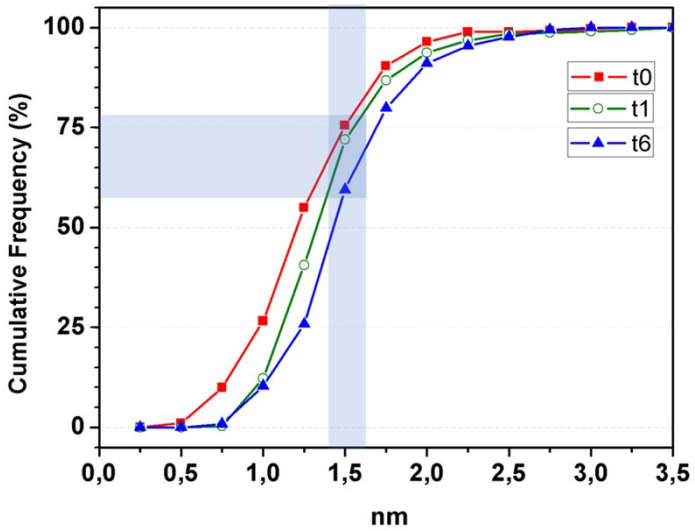

Figure S4. TEM images at ROI 2a for the sample Pt24 across ILTEM analysis at t0, t1 and t6

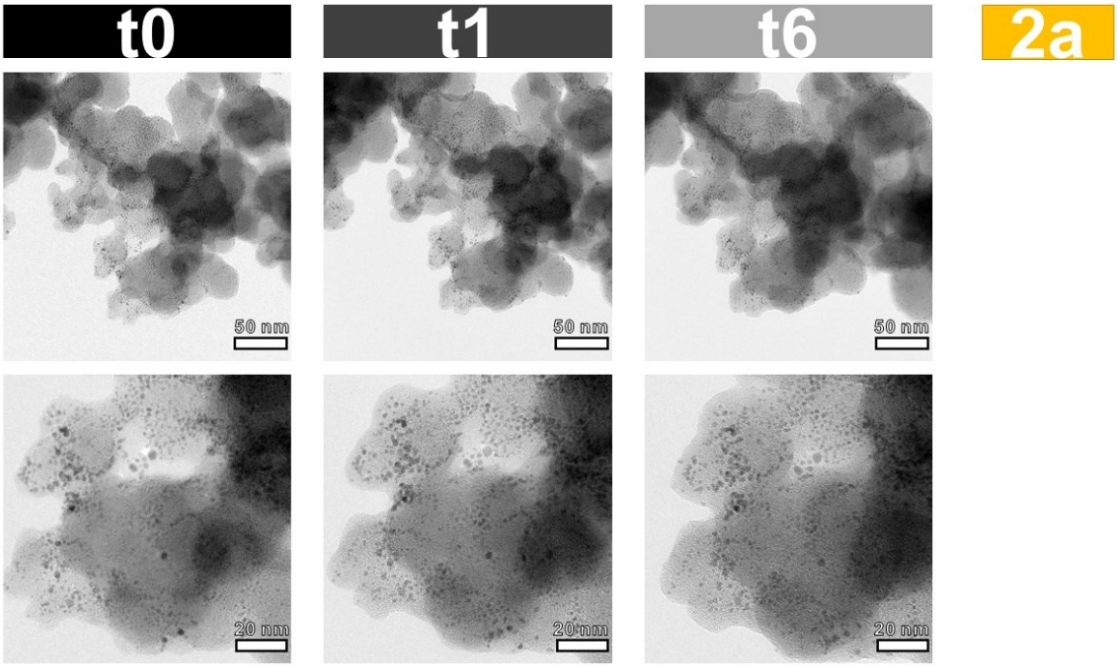

Figure S5. TEM images at ROI 2b for the sample Pt24 across ILTEM analysis at t0, t1 and t6

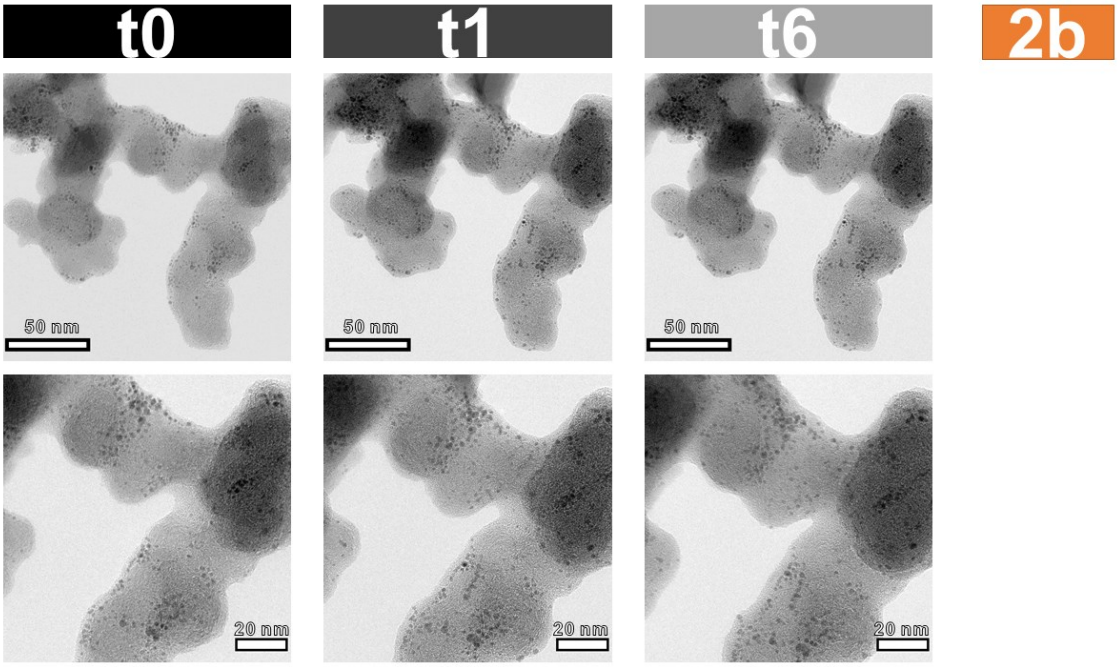

Figure S6. TEM images at ROI 3a for the sample Pt24 across ILTEM analysis at t0, t1 and t6

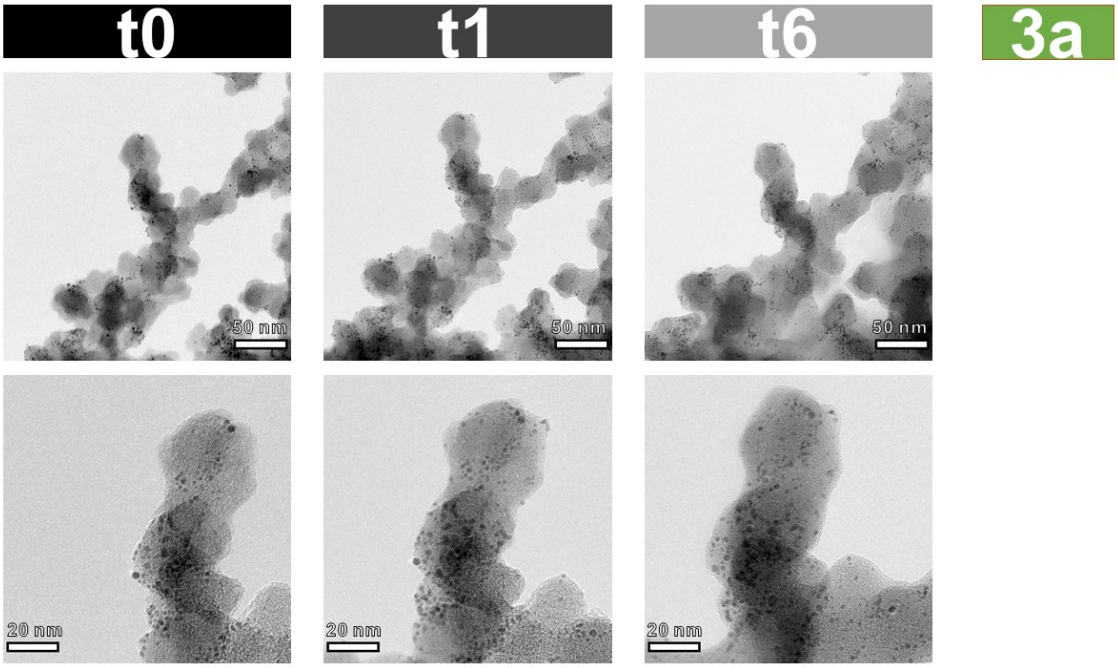

Figure S7. TEM images at ROI 4a for the sample Pt24 across ILTEM analysis at t0, t1 and t6

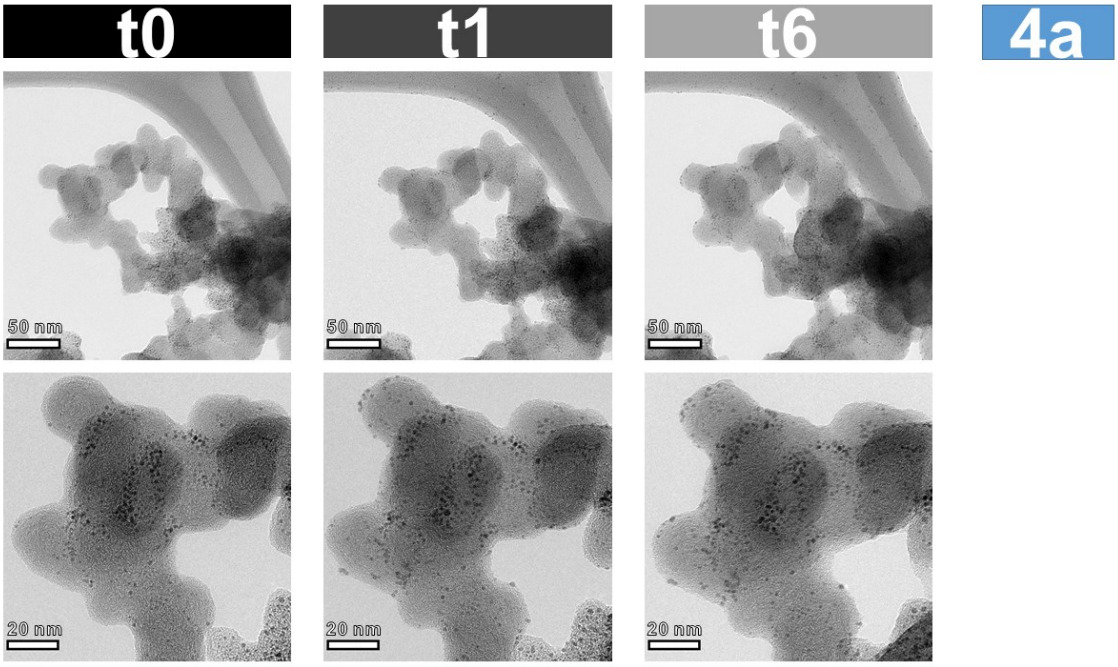

Figure S8. **a**) EXAFS spectrum at the Pt L_{III}-edge of Pt24: red dots: experimental; dashed line: fit according to the structural model described in text; blue dashed line: contribution of the carbon shell; yellow dashed line: contribution of the Pt shell. **b**) Fourier Transform of the EXAFS shown in a, with the same color code. **c**) EXAFS spectrum at the Pt L_{III}-edge of TrPt24: color code is the same as in a; **d**) Fourier Transform of the EXAFS shown in c, with the same color code.

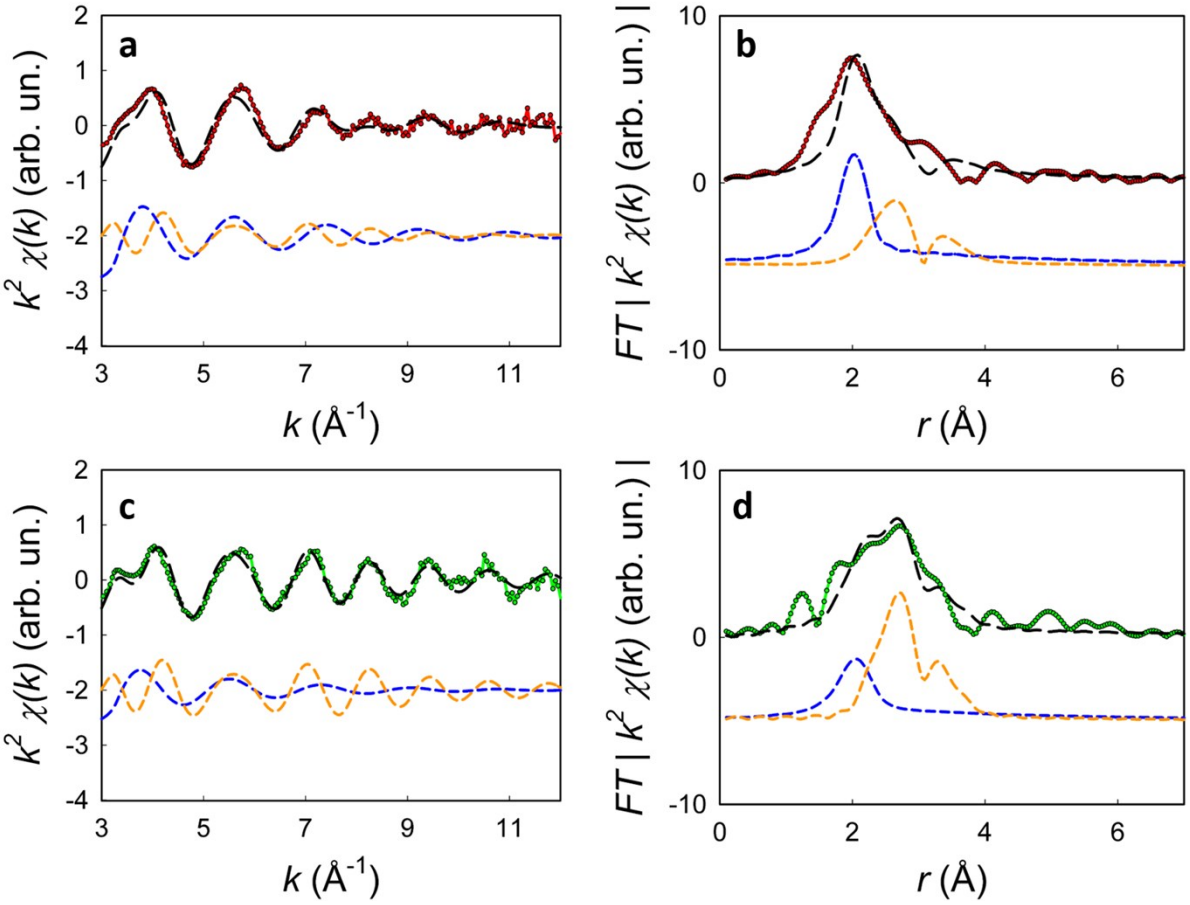

Table S1. Results of the Rietveld Refinements and of the WH analysis

	Pt12	TrPt12	Pt24	TrPt24
Space group	Fm-3m	Fm-3m	Fm-3m	Fm-3m
a / Å	3.998(3)	3.915(1)	3.917(1)	3.9076(5)
Adp / Å^2	0.016(3)	0.0086(6)	0.0127(8)	0.0076(4)
Rp	0.0268	0.0380	0.0307	0.0274
R(F^2)	0.0317	0.0466	0.0455	0.0135
Dv / Å	≈11	≈27	≈12	≈22
ε	0.0406	0.0044	0.0268	0.0081

Table S2. Results for PDF analysis in the 2-8 Å range. Dv values have been estimated using a wider fitting range (see main text for detail)

	Pt12	TrPt12	Pt24	TrPt24
a / Å	3.9421(2)	3.9236(4)	3.9118(1)	3.9146(2)
adp / Å^2	0.0237(1)	0.0109(1)	0.0162(1)	0.0113(1)
Dv / Å	13(2)	34(2)	15(1)	21(1)
Rw	0.470	0.178	0.210	0.108

Table S3. Half wave potentials at 1600 RPM, ORR onset potentials, number of exchanged electrons and ECSA values. Onset Potentials have been obtained by the cross-point between the x-axis and the extension of the straight line in the region of mixed current. See the arrow in Figure 7A.

sample	$E_{½}$ vs RHE @ 1600 RPM / V	E_{onset} vs RHE / V	Number of electrons	ECSA / $m^2 \cdot g^{-1}$
Pt24	0.905	1.021	4.04 ± 0.15	40.0
TrPt24	0.868	1.017	4.01 ± 0.05	9.3
Pt12	0.861	1.008	4.47 ± 0.12	21.7
TrPt12	0.868	1.019	4.07 ± 0.08	20.7
Pt/C	0.866	0.994	3.89 ± 0.04	7.2