Supporting Information

The impact of ligand chain length on HER performance of atomically precise $Pt_6(SR)_{12}$ nanoclusters

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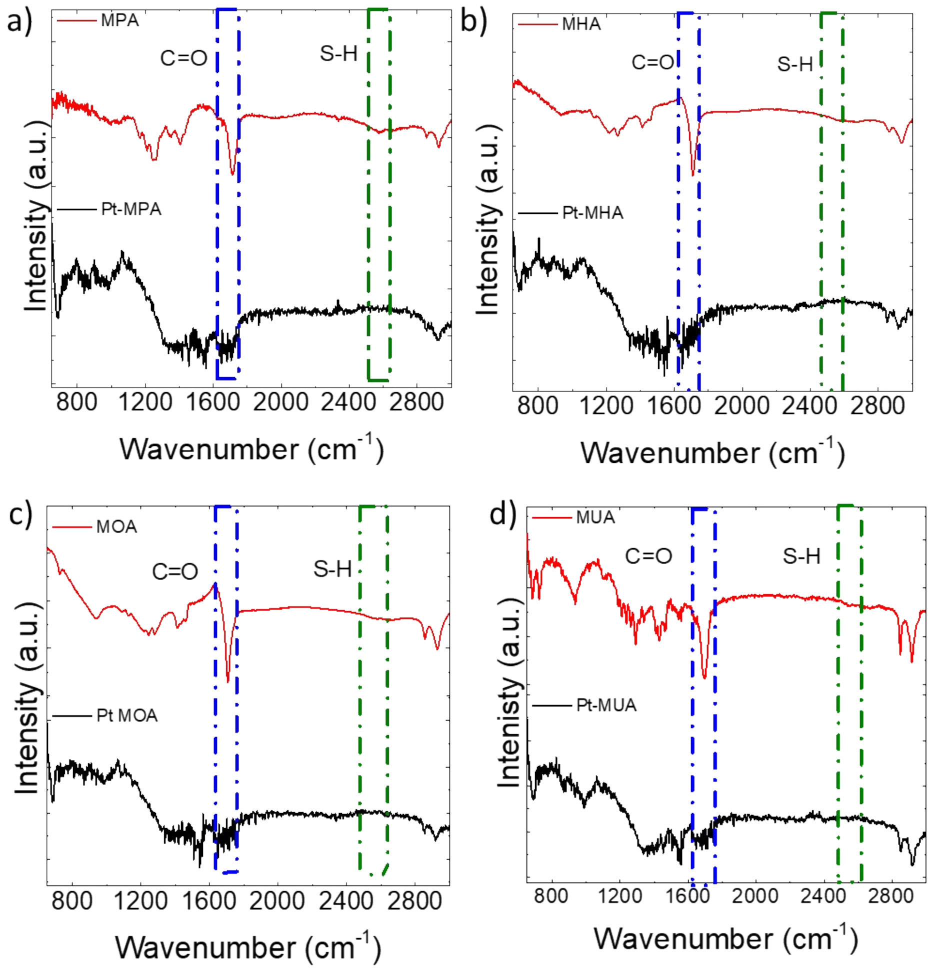

Fig. 1 FT-IR spectra of a) MPA and $Pt_6(MPA)_{12}$ NCs, (b) MHA and $Pt_6(MHA)_{12}$ NCs, (c) MOA and $Pt_6(MOA)_{12}$ NCs, (d) MUA and $Pt_6(MUA)_{12}$ NCs.

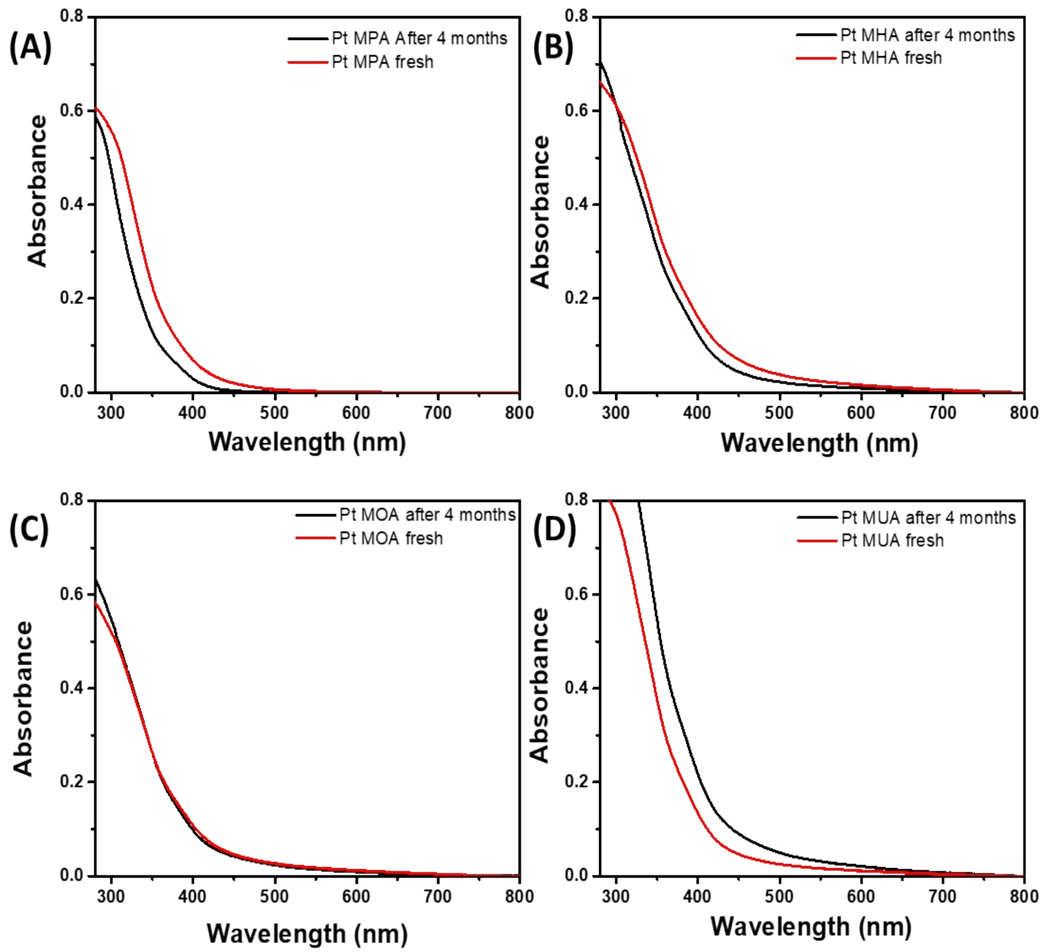

Fig. S2 UV-Vis spectra of as-prepared Pt NCs were recorded after fresh synthesis and after four months.

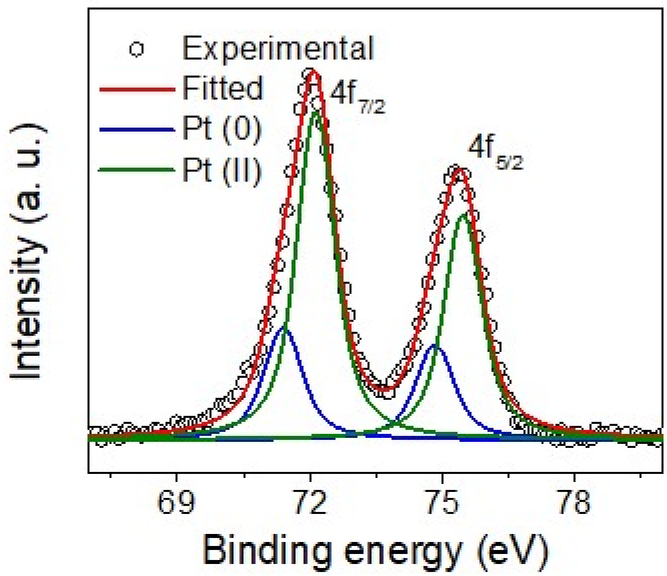

Fig. S3 The deconvolution of Pt 4f XPS spectrum of $Pt_6(MPA)_{12}$ NCs.

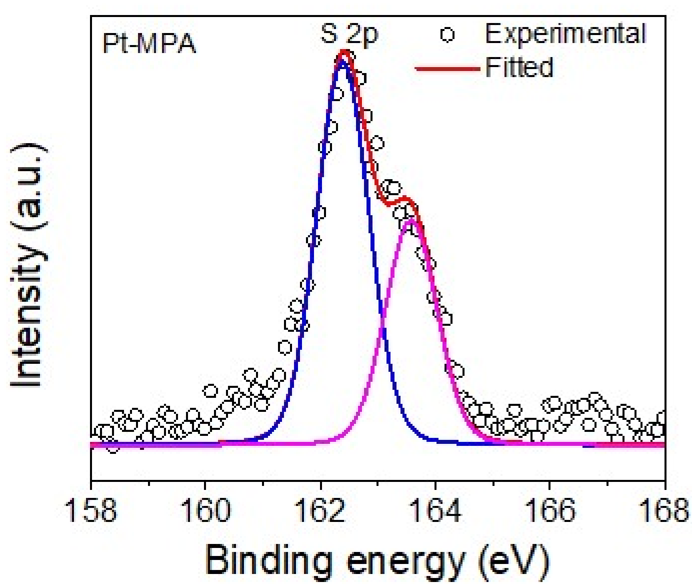

Fig. S4 The deconvolution of S 2p XPS spectrum of $Pt_6(MPA)_{12}$ NCs.

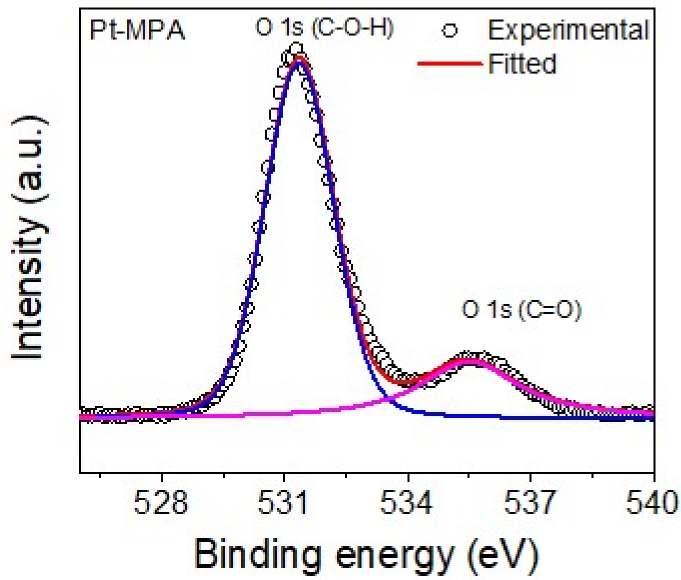

Fig. S5 The deconvolution of O 1s XPS spectrum of $Pt_6(MPA)_{12}$ NCs.

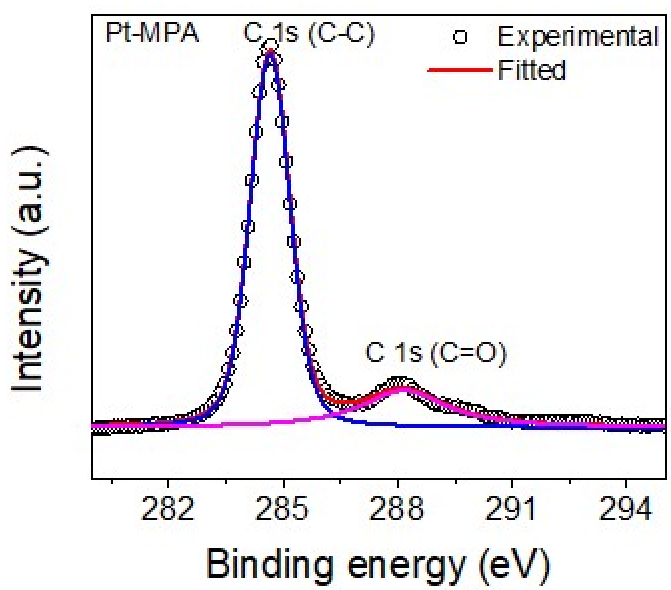

Fig. S6 The deconvolution of C1s XPS spectrum of $Pt_6(MPA)_{12}$ NCs.

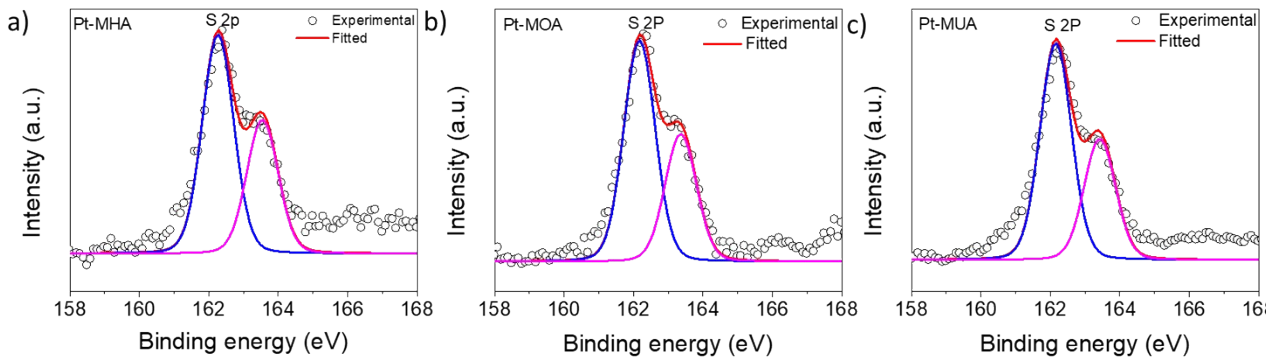

Fig. S7 The deconvolution of S 2p XPS spectrum of (a) $Pt_6(MHA)_{12}$ NCs, (b) $Pt_6(MOA)_{12}$ NCs, (c) $Pt_6(MUA)_{12}$ NCs.

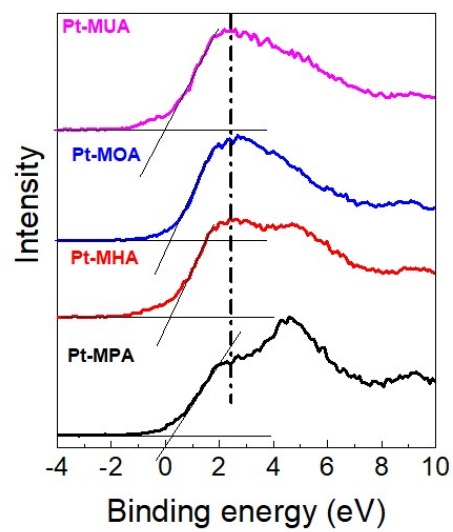

Fig. S8 Valence band spectra of $Pt_6(MPA)_{12}$ NCs, $Pt_6(MHA)_{12}$ NCs, $Pt_6(MOA)_{12}$ NCs, and $Pt_6(MUA)_{12}$ NCs depicting the method to locate VBM.

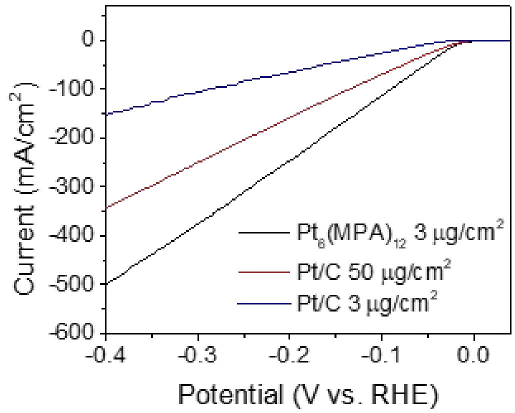

Fig. S9 HER polarization curve of $Pt_6(MPA)_{12}$ NCs and commercial Pt/C at different mass loading.

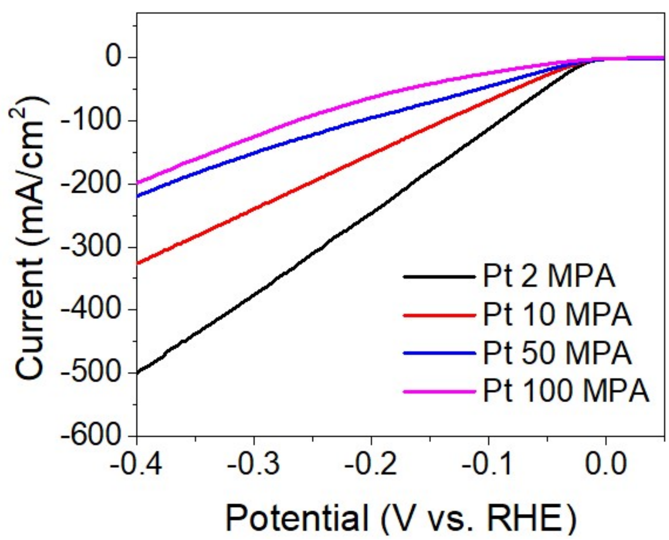

Fig. S10 HER polarization curves of Pt NCs synthesized using 2, 10, 50, and 100 µl of MPA ligand.

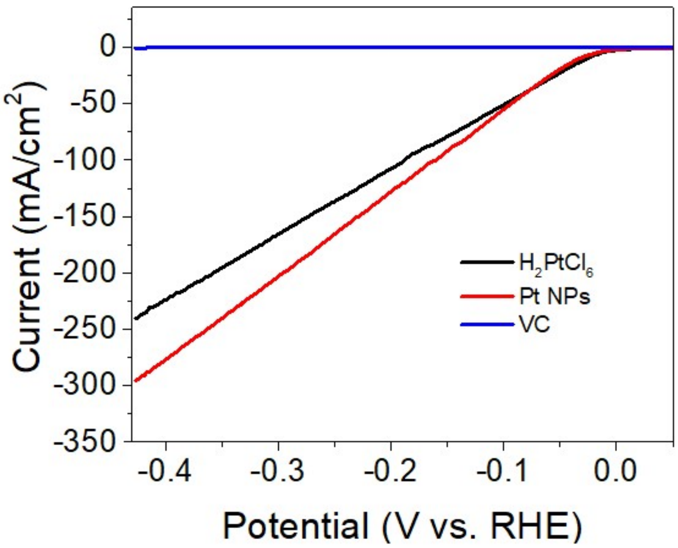

Fig. S11 HER polarization curves of Pt samples synthesized without MPA ligand (Pt NPs) and using only H_2PtCl_6 on Vulcan carbon (Pt content kept same).

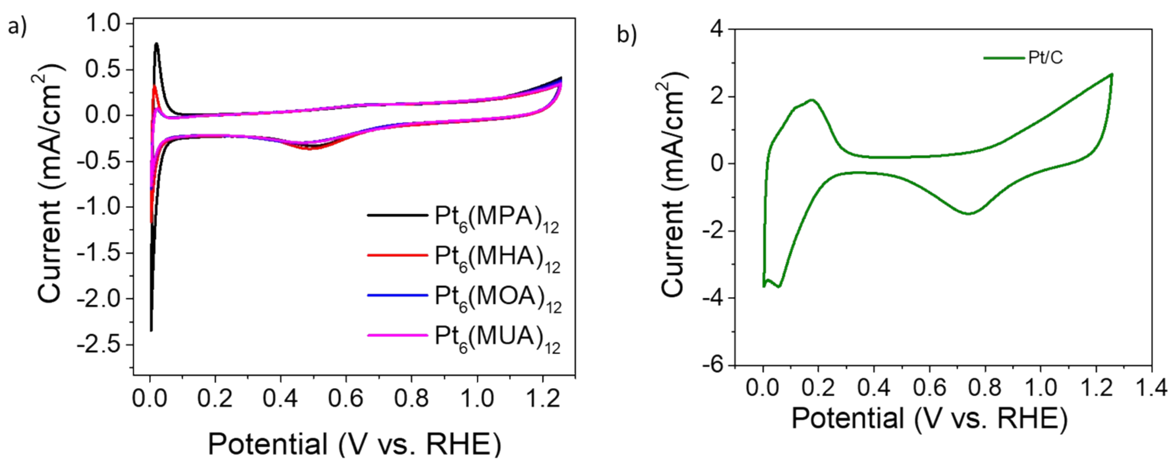

Fig. S12 Cyclic voltammograms of (a) $Pt_6(SR)_{12}$ NCs (b) Pt/C recorded in Ar saturated 0.5 M H_2SO_4 at a sweep rate of 50 mV/s.

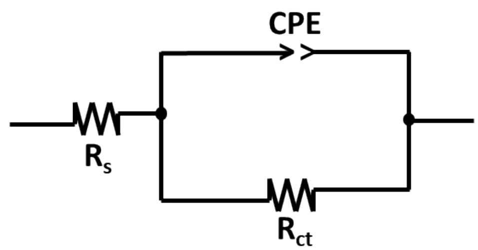

Fig. S13 Standard Randel's equivalent circuit is used to fit the Nyquist plot.

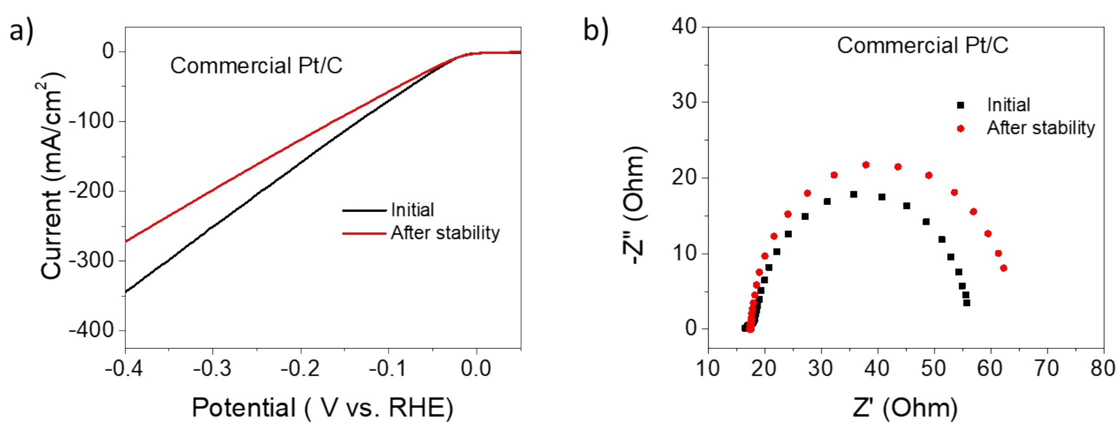

Fig. S14 (a) HER polarization curve of Pt/C was recorded before and after the catalysis, and (b) Nyquist plot of Pt/C was recorded before and after the catalysis.

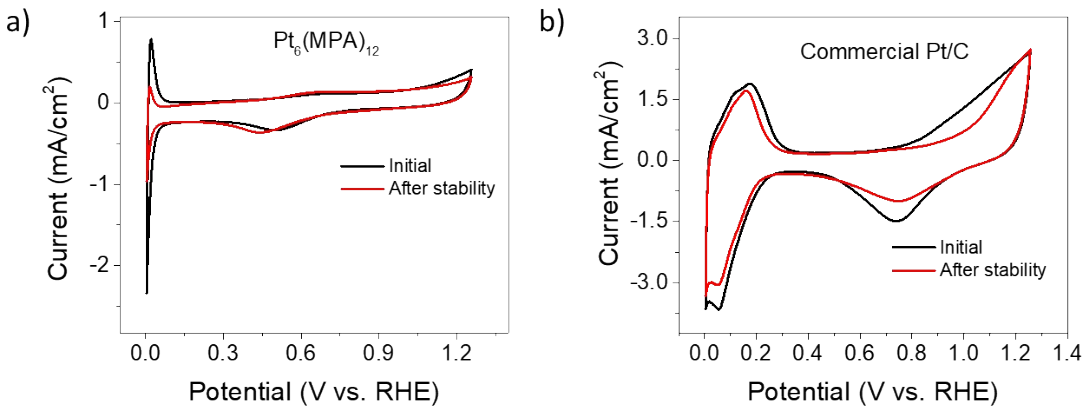

Fig. S15 Cyclic voltammograms of (a) $Pt_6(MPA)_{12}$ NCs recorded before and after the catalysis, (b) Pt/C recorded before and after the catalysis.

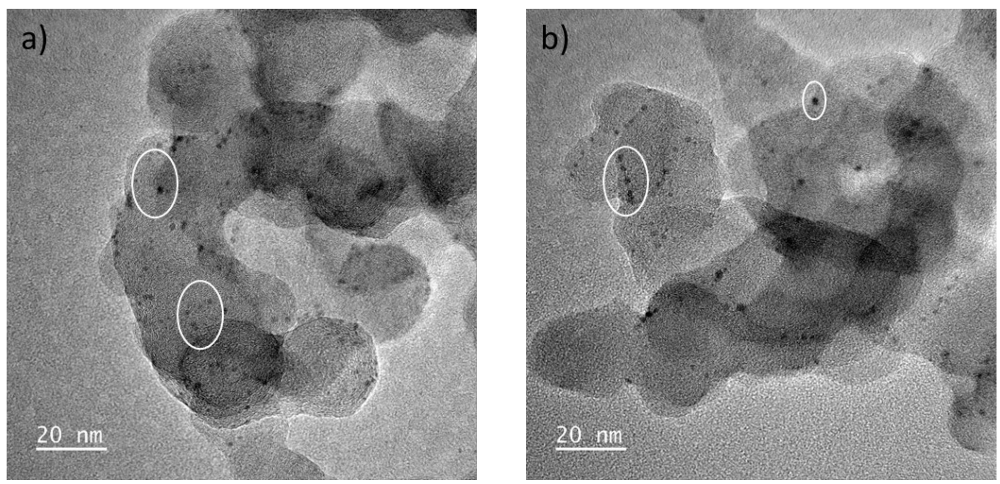

Fig. S16 TEM images of $Pt_6(MPA)_{12}$ NCs were recorded after the catalysis. The highlighted region shows that the $Pt_6(MPA)_{12}$ NCs remains strongly intact with the Vulcan Carbon after catalysis.

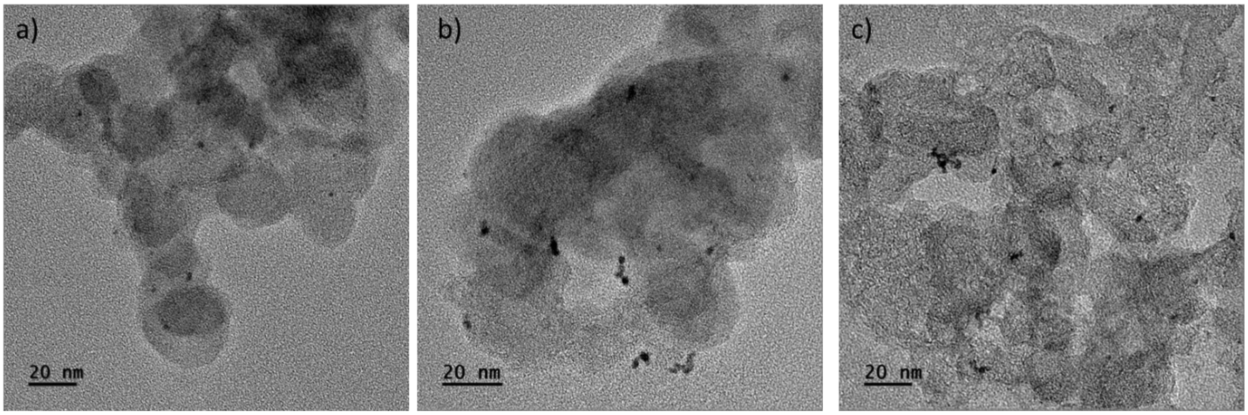

Fig. S17 TEM images of a) $Pt_6(MHA)_{12}$, b) $Pt_6(MOA)_{12}$, b) $Pt_6(MUA)_{12}$ recorded after catalysis.

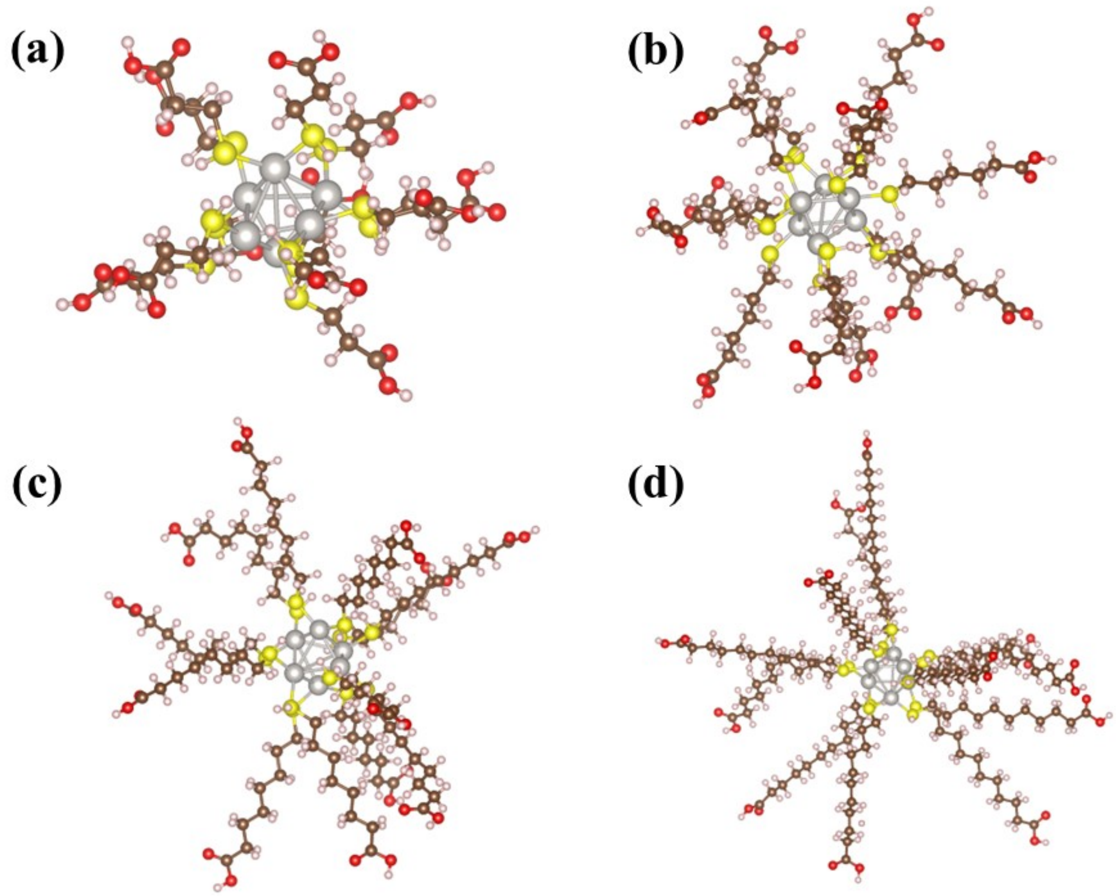

Fig. S18 The optimized geometries of the catalysts (a) $Pt_6(MPA)_{12}$ NCs, (b) $Pt_6(MHA)_{12}$ NCs, (c) $Pt_6(MOA)_{12}$ NCs, (d) $Pt_6(MUA)_{12}$ NCs. The grey, yellow, brown, red, and white balls represent Pt, S, C, O, and H atoms, respectively.

Table S1. Comparison of electrocatalytic HER performance of the $Pt_6(MPA)_{12}$ with other Pt-based *state-of-the-art* electrocatalysts developed recently.

Catalyst	Electrolyte	Pt loading amount (µg/cm^2)	Overpotential at 10 mA/cm^2 (mV)	Tafel slope (mV/dec)	Reference
$Pt_6(MPA)_{12}$	0.5 M H_2SO_4	2.55	19	30	This work
Pt_5/HMCS	0.5 M H_2SO_4	7.6	20.7	28.3	[1]
Pt_1/Mesoporous C	0.5 M H_2SO_4	10	26	NA	[2]
Pt1/OLC	0.5 M H_2SO_4	1.4	38	36	[3]
Mo_2TiC_2 Tx–PtSA	0.5 M H_2SO_4	12	30	30	[4]
Pt-SAs/WS_2	0.5 M H_2SO_4	10	32	28	[5]
Pt_1/N-C	0.5 M H_2SO_4	6.25	19	14.2	[6]
$Pt_1O_1/Ti_{1-x}O_2$	0.5 M H_2SO_4	1.27	22.2	31	[7]

Pt-Ni ASs	0.5 M H_2SO_4	17	27.7	27	[8]
Pt_3Co@NCNT	0.5 M H_2SO_4	100	42	27.2	[9]
Pt-SA/ML-WO_3	0.5 M H_2SO_4	1.1	22	27	[10]
EG-Pt/ CoP-1.5	0.5 M H_2SO_4	1.53	21	42.5	[11]
Pt-PVP/ TNR@GC	0.5 M H_2SO_4	21.8	21	27	[12]
Pt1/NMHCS	0.5 M H_2SO_4	6.55	41	56	[13]
PtW NPs/C	0.5 M H_2SO_4	20.8	19.4	27.8	[14]
PtW_6O_{24}/C	0.5 M H_2SO_4	NA	22	29.8	[15]
Pt SASs/AG	0.5 M H_2SO_4	31.1	12	29	[16]
Pt/NGNs	0.5 M H_2SO_4	1.6	38	29	[17]
Pt_3Ni_2 NWs-S/C	0.5 M H_2SO_4	15.3	28	NA	[18]

Pt@DNA−GC	0.5 M H_2SO_4	15	26	30	[19]
Pt1/MC	0.5 M H_2SO_4	10	25	26	[20]
Pt1/NPC	0.5 M H_2SO_4	3.8	25	28	[21]
Pt1/NMC	0.5 M H_2SO_4	10	29	26	[22]
PtCoFe@CN	0.5 M H_2SO_4	13.11	45	32	[23]
400-SWNT/Pt	0.5 M H_2SO_4	19.4	27	38	[24]
200-SWNT/Pt	0.5 M H_2SO_4	5.6	40	38	[24]
Pt-MoS_2	0.5 M H_2SO_4	7.28	38	25	[25]
Ti-based SAL/SAB Pt	0.5 M H_2SO_4	4.5	19	25.9	[26]
ALD50Pt/NGNs	0.5 M H_2SO_4	1.6	39	29	[17]
Pt/NiS@Al_2O_3	0.5 M H_2SO_4	16	34	35	[27].

Pt-Au_{25} NCs	0.1 M H_2SO_4	0.8	117	86	[28]
Pt NCs/rgo	0.5 M H_2SO_4	0.8 wt%	67	46	[29]

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