Supporting information of the manuscript:

Controlled assembly and single electron charging of monolayer protected Au_{144} clusters: electrochemistry and scanning tunneling spectroscopy study

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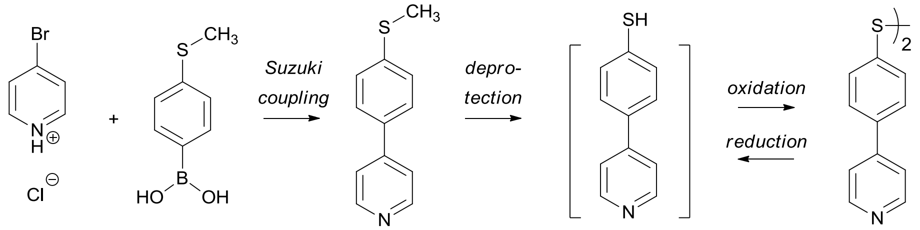
Synthesis and characterization of the ligand molecules:

The ligand 1,2-bis(4'-(pyridin-4''-yl)-phenyl)disulfane **1** was synthesized follwing slightly modified literature procedures.[1,2] The 4-bromopyridine hydrochloride (**2**) and 4-(methylthio)-phenylboronoic acid (**3**) were coupled in a Suzuki reaction providing 4-(4-(methylthio)phenyl)-pyridine (**4**) in good yields. Treatment of **4** with an alkylthiolate in dimethylformamide (DMF) gave the deprotected 4-(pyridin-4'-yl)benzenethiol **5** as free thiophenol derivative. In the presence of oxygen, **5** oxidized quickly to the stable disulfide **1**. It is noteworthy that under the applied reductive conditions used for the synthesis of the Au MPCs, **1** is rduced back to the free thiophenol **5**.



2 **3** **4** **5** **1**

General remarks: All chemicals were commercially available and were used as received. 4-Bromopyridine hydrochloride was obtained from Fluorochem. 4-(Methylthio)phenylboronic acid, sodium 2-methyl-2-propanethiolate, tetraoctylammonium bromide (TOABr, >98%) sodium borohydride ($NaBH_4$, 96%) and dimethylformamide (DMF) were obtained from Aldrich. Tetrakis(triphenylphosphine)palladium (0), 99%, tetrabutylammonium bromide (TBABr, 99%), 1-hexanethiol (96%) and tetrachloroauric(III) acid ($HAuCl_4$ H_2O, >49% Au) were purchased from Acros. 1,2-Dimethoxyethane (DME, 99%) was obtained from Alfa Aesar, HPLC solvents (acetone, methanol and dichloromethane) were purchased from Baker.

Suzuki coupling: 4-Bromopyridine hydrochloride (2.44 mmol, 1 eq.), 4-(methylthio)phenyl-boronic acid (2.44 mmol, 1 eq.) together with KOH (12.2 mmol, 5 eq.) as base, TBABr (12 mol%) as phase transfer catalyst, tetrakis(triphenylphosphine)palladium (6 mol%) as catalyst and DME (15 ml) and water (5 ml) as solvents were put in the reaction vessel. The reaction mixture was degassed by bubbling argon through the solution for 10 minutes before heating it up by microwave to 160 °C for 1.5 h. After aqueous work up and extraction with diethylether, the combined organic phases were washed with water and brine before drying over Na_2SO_4. Evaporation of the solvent provided the crude product which was purified by sublimation to provide 4-(pyridin-4'-yl)thioanisole in 97 % yield as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 6.2 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 6.3 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.42, 147.71, 140.45, 134.64, 127.36, 126.79, 121.28, 15.60; GC-MS (EI) m/z: 201.0 $[M]^+$, 186.0 $[M\text{-}Me]^+$; MS (DART-EI) m/z: 201.8 $[M+H]^+$, 403.0 $[2M+H]^+$.

Deprotection: 4-(Pyridin-4'-yl)thioanisole (1.31 mmol, 1 eq.) and sodium 2-methyl-2-propanethiolate (3.6 mmol, 2.8 eq.) were dissolved in dry DMF (10 ml), degassed by bubbling argon through the solution for 10 minutes before heating the mixture to 160 °C for 4 h. After

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[1] A. Gallardo-Godoy, M. I. Torres-Altoro, K. J. White, E. L. Barker and D. E. Nichols, *Bioorg. Med. Chem.*, **2007**, *15*, 305-311.

[2] H. Qian and R. Jin, *Chem. Mater.*, **2011**, *23*, 2209-2217.

cooling to room temperature, the solution was poured on ice and the pH was adjusted to 6 with aq. HCl (1M). Extraction with CH_2Cl_2 followed by drying the combined organic phases over Na_2SO_4 and evaporation of the solvent under reduced pressure provided the crude product, which was further purified by column chromatography (SiO_2, EtOAc/CH_2Cl_2: 4/1) to yield in 4-(pyridin-4’-yl)benzenethiol (51%) as yellow solid. The ligand is prone to form disulfides in the presence of oxygen. As the disulfide is cleaved in the reducing conditions during Au particle formation, we used the disulfide 1,2-bis(4’-(pyridin-4’’-yl)phenyl)disulfane for the synthesis of the Au MPCs. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (d, J = 6.1 Hz, 4H), 7.62 (d, J = 6.9 Hz, 8H), 7.50 – 7.43 (m, 4H); ^{13}C NMR (101 MHz, CDCl3) δ = 133.03, 132.29, 132.19, 131.99, 128.70, 128.58.

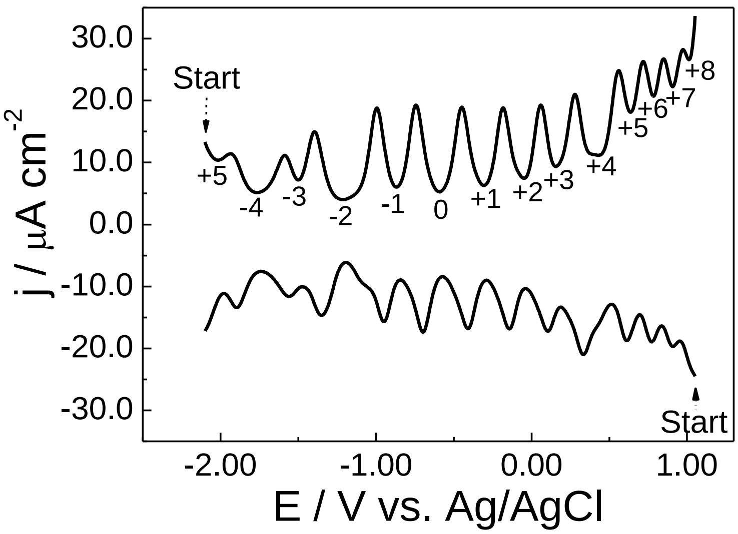


Fig. S1 DPV of a Pt electrode in a 0.1 mM solution of Au_{144} MPCs dissolved in a mixture of toluene and acetonitrile (2:1) containing 0.1 M of $TBAPF_6$ as supporting electrolyte. Pulse width: 60 ms, pulse height: 50 mV, period: 200 ms, scan rate: 20 mVs^{-1}.

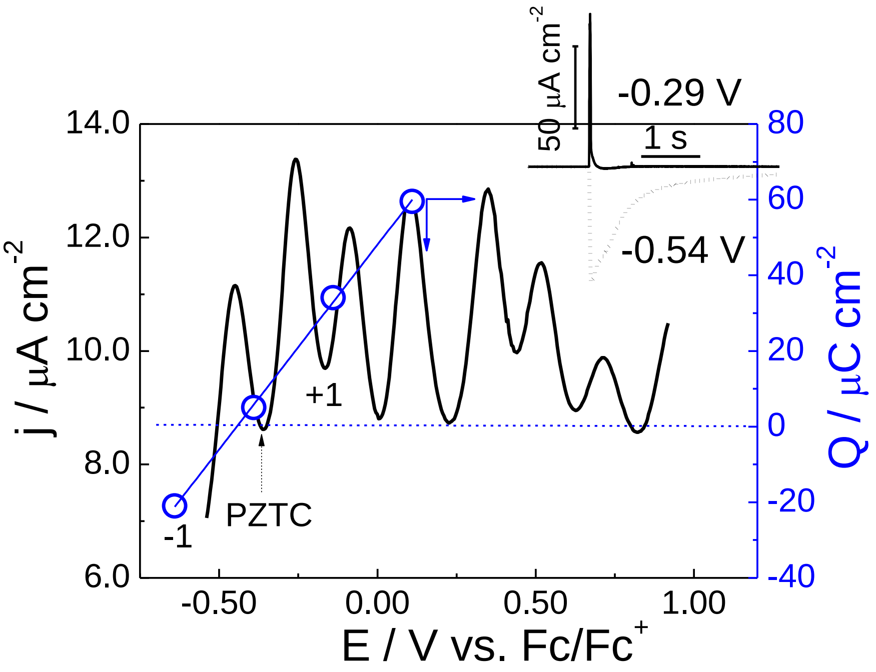
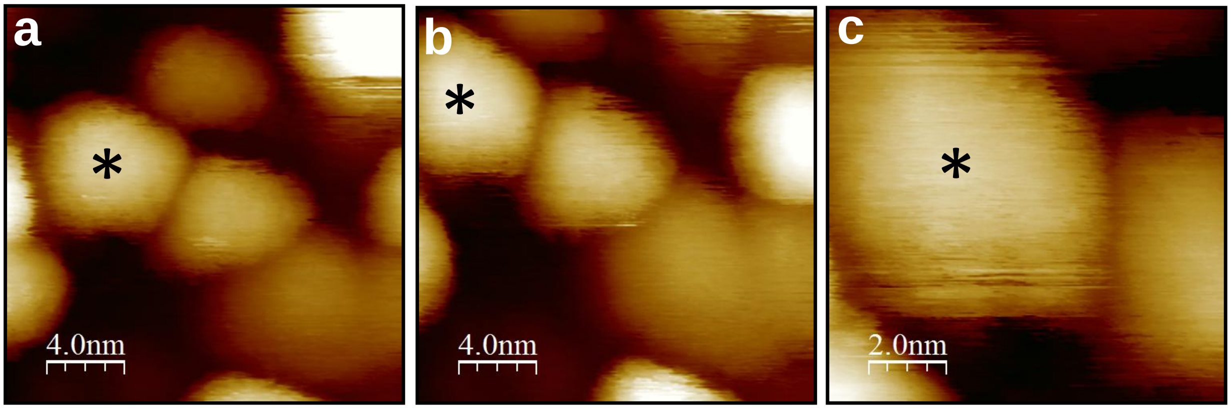


Fig. S2 DPV of a self-assembled layer of Au_{144} MPCs on a Pt(111) electrode in $[C_6C_1Im][FEP]$ ionic liquid. The inset shows the current transient curves at -0.29 V and -0.54 V vs. Fc/Fc$^+$. Pulse width: 60 ms, pulse height: 50 mV, period: 200 ms, scan rate: 20 mVs^{-1}.



20 nm × 20 nm

20 nm × 20 nm

10 nm × 10 nm

Fig. S3 In-situ STM images of $Au_{144}(C_6S)_{60}(C_{11}H_8NS)_6$ MPCs on a Pt(111) surface in 0.1 M $NaClO_4$. Scanning aize (**a**) 20 × 20 nm^2, (**b**) 20 × 20 nm^2, (**c**) 10 × 10 nm^2. Set point current I_{set}: 60 pA, bias voltage V_{bias}: +0.3 V, E_S: -0.6 V, E_t: +0.3 V.

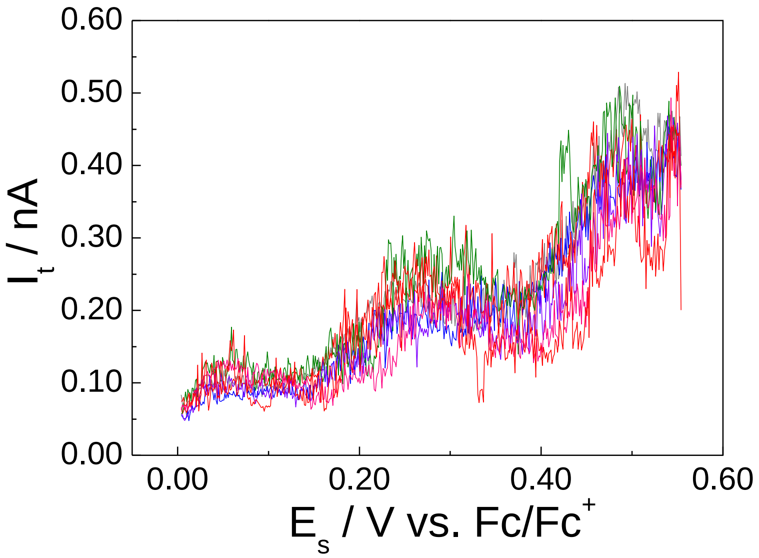


Fig. S4 Overlay of the STS traces: constant bias tunneling current-voltage response of a single Au_{144} cluster obtained in 0.1 M $NaClO_4$ on a Pt(111) surface; I_{set}: 60 pA, V_{bias}: +0.05 V, sweep rate 0.8 Vs^{-1}.

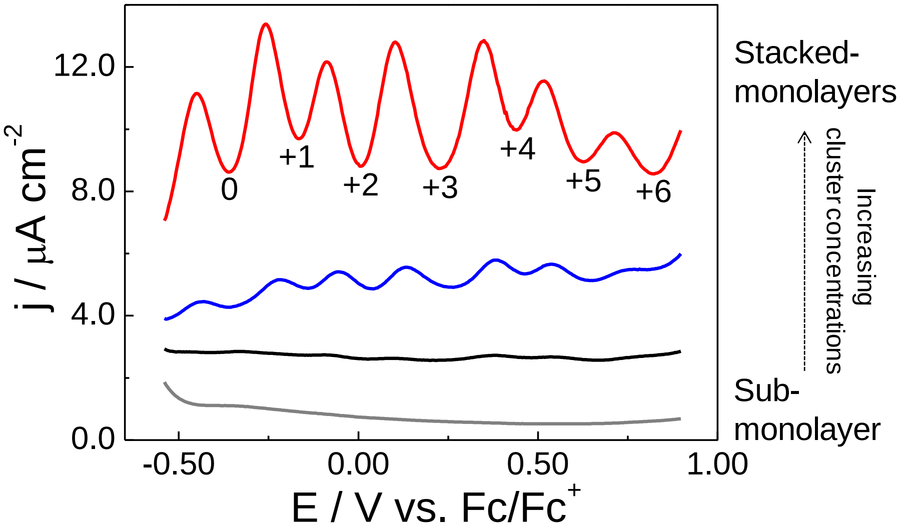


Fig. S5 DPV of a multilayer Au_{144} MPCs on a Pt(111) electrode in $[C_6C_1Im][FEP]$ ionic liquid. Pulse width: 60 ms, pulse height: 50 mV, period: 200 ms, scan rate 20 mVs^{-1}. The cluster concentration on the electrode surface was increased as shown in the figure.

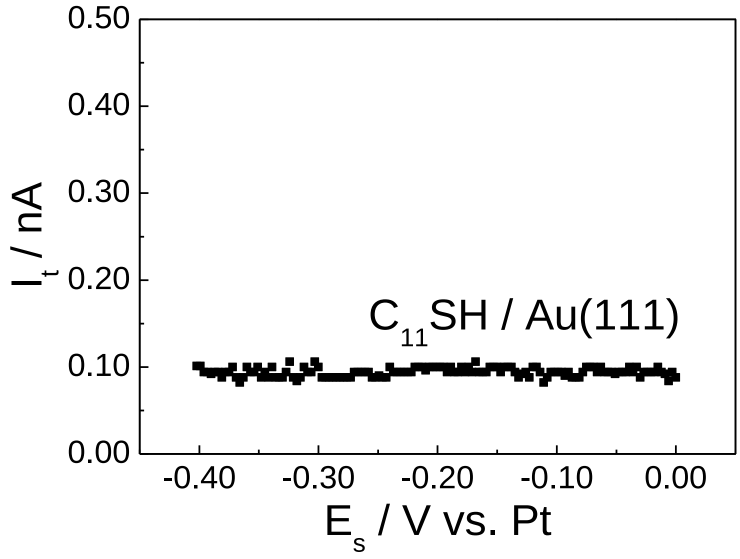


Fig. S6 Constant bias tunneling current-voltage response of a self-assembled monolayer of 1-undecanethiol SAM on a Au (111) surface recorded in the aqueous solution of 0.1 M $HClO_4$. I_{set}: 0.1 nA, V_{bias}: +0.1 V, E_s: -0.5 V, E_t: -0.4 V, sweep rate: 0.6 Vs^{-1}. The represented data is averaged from 25 individual runs.

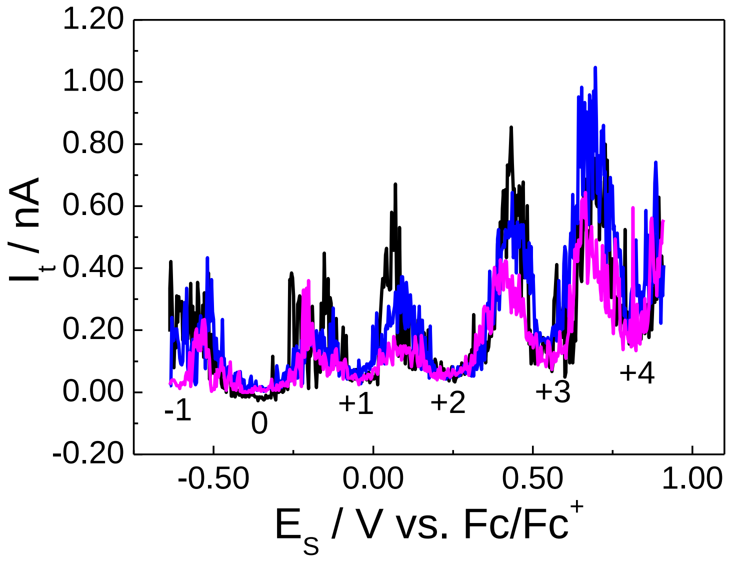


Fig. S7 Overlay of the STS traces: constant bias tunneling current-voltage response of a single cluster on a Pt(111) surface in $[C_6C_1Im][FEP]$ IL. I_{set}: 50 pA, V_{bias}: +0.10 V, sweep rate 0.8 Vs^{-1}**.**

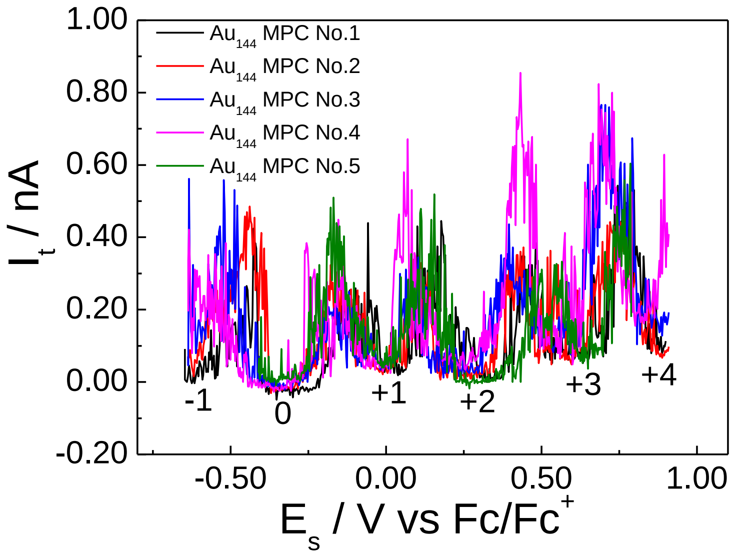


Fig. S8 Overlay of the STS traces obtained from different Au_{144} MPCs in [C_6C_1Im][FEP. I_{set}: 50 pA, V_{bias}: +0.10 V, sweep rate 0.8 V s^{-1}**.**

Table S1. STS peak potential spacing (ΔE) and cluster capacitance (c) values measured in [C_6C_1Im][FEP] ionic liquid. The averaged values for ΔE and C are shown in Table 1 of the main paper.

Charge state	**ΔE** / V (cp)$^{a)}$	**C** / aF (cp)	**ΔE** / V (i)$^{b)}$	**C** / aF (i)
$\Delta E_{0/+1}$	0.253	0.634	0.356	0.451
$\Delta E_{+1/+2}$	0.275	0.583	0.220	0.722
$\Delta E_{+2/+3}$	0.390	0.411	0.288	0.558
$\Delta E_{+3/+4}$	0.257	0.625	0.208	0.742
$\Delta E_{+4/+5}$	---	---	0.322	0.498

$^{a)}$ CP = closely packed; $^{b)}$ i = isolated

Table S2. STS and DPV peak potential spacing (ΔE) and cluster capacitance (c) values measured for the Au_{144} MPCs in different electrolytes. The represented STS data is for *isolated particle* measurements. The averaged values for ΔE and C are shown in Table 1 of the main paper.

Electrolyte	Charge state	DPV		STS (i)[a]	
		ΔE / V	C / aF	ΔE / V	C / aF
CH_3CN (0.01 M BTPPA-TPFB)	$\Delta E_{0/+1}$	0.181	0.884	Note[b]	
	$\Delta E_{+1/+2}$	0.185	0.864		
	$\Delta E_{+2/+3}$	0.198	0.810		
	Average	0.188	0.852		
H_2O (0.1 M $NaClO_4$)	$\Delta E_{+1/+2}$	0.132	1.214	---	---
	$\Delta E_{+2/+3}$	0.135	1.183	0.211	0.759
	$\Delta E_{+3/+4}$	---	---	0.227	0.704
	Average	0.134	1.198	0.219	0.730
$[C_6C_1Im][FEP]$	$\Delta E_{0/+1}$	0.192	0.835	0.361	0.444
	$\Delta E_{+1/+2}$	0.171	0.939	0.245	0.653
	$\Delta E_{+2/+3}$	0.189	0.843	0.333	0.481
	$\Delta E_{+3/+4}$	0.247	0.649	0.247	0.650
	$\Delta E_{+4/+5}$	0.167	0.959	---	---
	$\Delta E_{+5/+6}$	0.197	0.813	---	---
	Average	0.194	0.840	0.297	0.540

[a] i = isolated; [b] Data not available. Due to the fast evaporation of the CH_3CN solvent the STS measurements cannot be done in this solvent.