Electrocrystallization of monolayer – protected gold clusters: opening the door to quality, quantity and new structures

Sabrina Antonello,[‡] Tiziano Dainese,[‡] Fangfang Pan,[†,⊥] Kari Rissanen,[*,†] and Flavio Maran*,[‡,§]

‡Department of Chemistry, University of Padova, via Marzolo 1, 35131 Padova, Italy
†Department of Chemistry, Nanoscience Center, University of Jyvaskyla, P.O. Box 35, 40014 Jyvaskyla, Finland
§Department of Chemistry, University of Connecticut, 55 North Eagleville Road, Storrs, Connecticut 06269, United States

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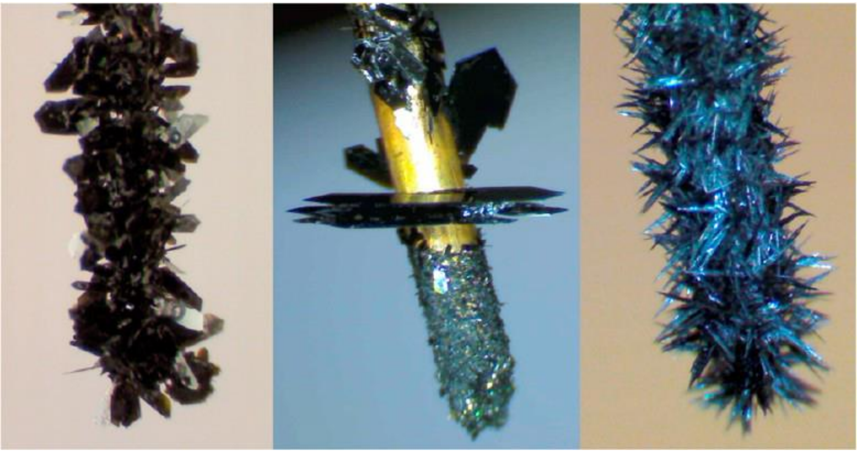

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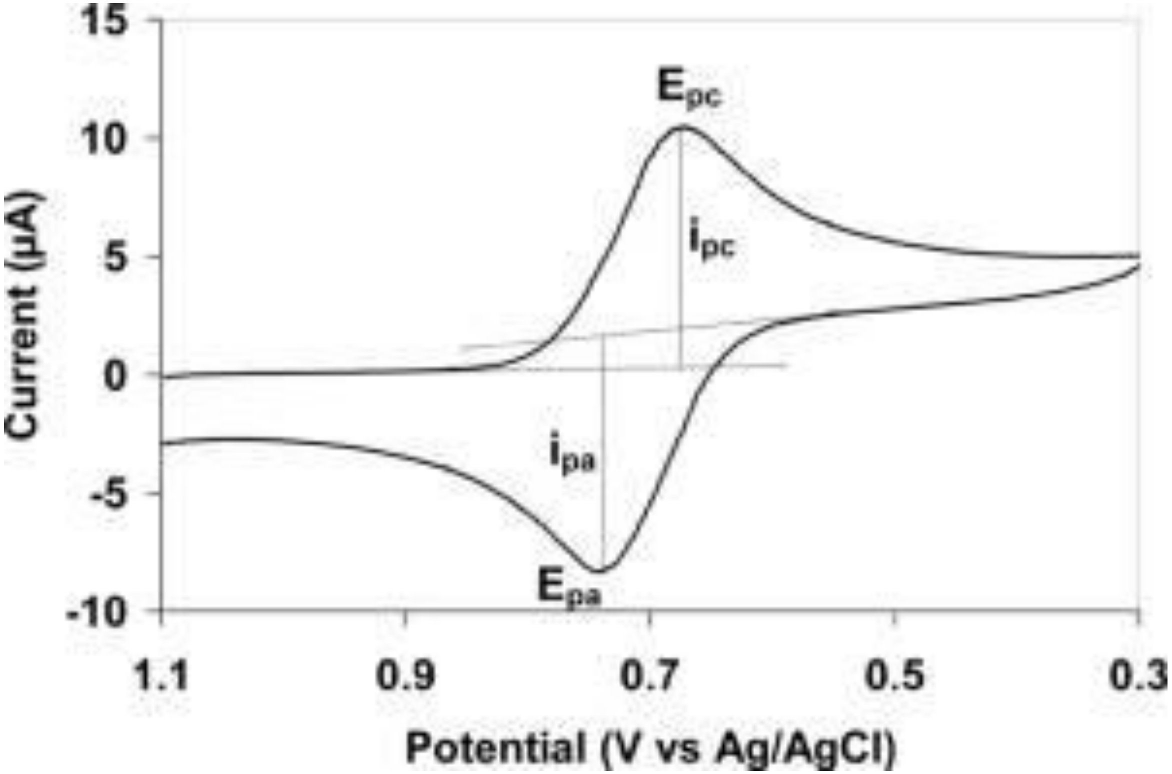
Electrocrystallization: A specialized application of electrolysis involves the growth of conductive crystals on one of the electrodes from oxidized or reduced species that are generated in situ.

Cyclic voltammetry (CV) is a type of potentiodynamic electrochemical measurement, where the working electrode potential is ramped linearly versus time.



Introduction:

- Knowledge of the single-crystal crystallographic structures indeed provides an invaluable insight into understanding the fascinating properties of MPCs as well as a starting point to develop theories, predict possible structures, and devise experimental methodologies suitable to expand the scope of these molecular systems.

- Despite of solving challenging structures, there are still cases that remain elusive or studies and applications that would require preparation of high-quality single crystals in large quantities.

- This points to the urge of developing a versatile strategy to prepare single crystals suitable for X-ray crystallographic analysis and solid-state applications.

- Electrochemistry has the advantage of controlling the potential of a metal substrate where solid materials can be deposited.

In this paper:

- Single crystals of thiolate-protected clusters can be grown in large quantity and very high quality by electrocrystallization.

- This method relies on the fact that charged clusters display a higher solubility in polar solvents than their neutral counterparts.

- Electrocrystallization of three known $Au_{25}(SR)_{18}^0$ clusters and a new cluster $Au_{25}(SnC_5H_{11})_{18}$, was described with effective yields.

- High quality single crystals made via this process is suitable for X-ray crystallographic analysis.

Experimental details:

- The electrochemical experiments were carried out under an Ar atmosphere, in a glass cell at room temperature.

- For CV, the working electrode was a glassy carbon microdisk (9.10×10^{-4} cm^2), Ag/AgCl served as the reference electrode in MeCN, its potential was determined to be 0.201 V against the KCl saturated calomel electrode (SCE) and counter-electrode was a Pt plate inserted into a glass holder separated from the analyte solution with a G3 glass frit and a plug of electrolyte saturated methylcellulose gel.

- We used a CHI 660c electrochemical workstation.

- For CV experiments, the feedback correction was applied to minimize the ohmic drop between the working and the reference electrodes.

- Pictures of the electrodeposited crystals were taken with a Firefly GT800 high-precision video microscope. For this purpose, some experiments were conducted by using a quartz cuvette as the electrochemical cell.

Results and discussion:

Electrocrystallization strategy :

(i) The initial and final oxidation states are chemically stable.

(ii) The solvent/electrolyte system must allow for dissolution of the initial charge state and grant insolubility of the electrochemically generated species.

(iii) The current density has to be adjusted to sufficiently low values, thereby favoring crystallization on the electrode body as opposed to causing random precipitation of insoluble powder at the bottom of the electrochemical cell.

(iv) Crystallization should lead to a fairly conductive material suitable to make the electrode process occurring on the growing crystals.

Results and discussion:

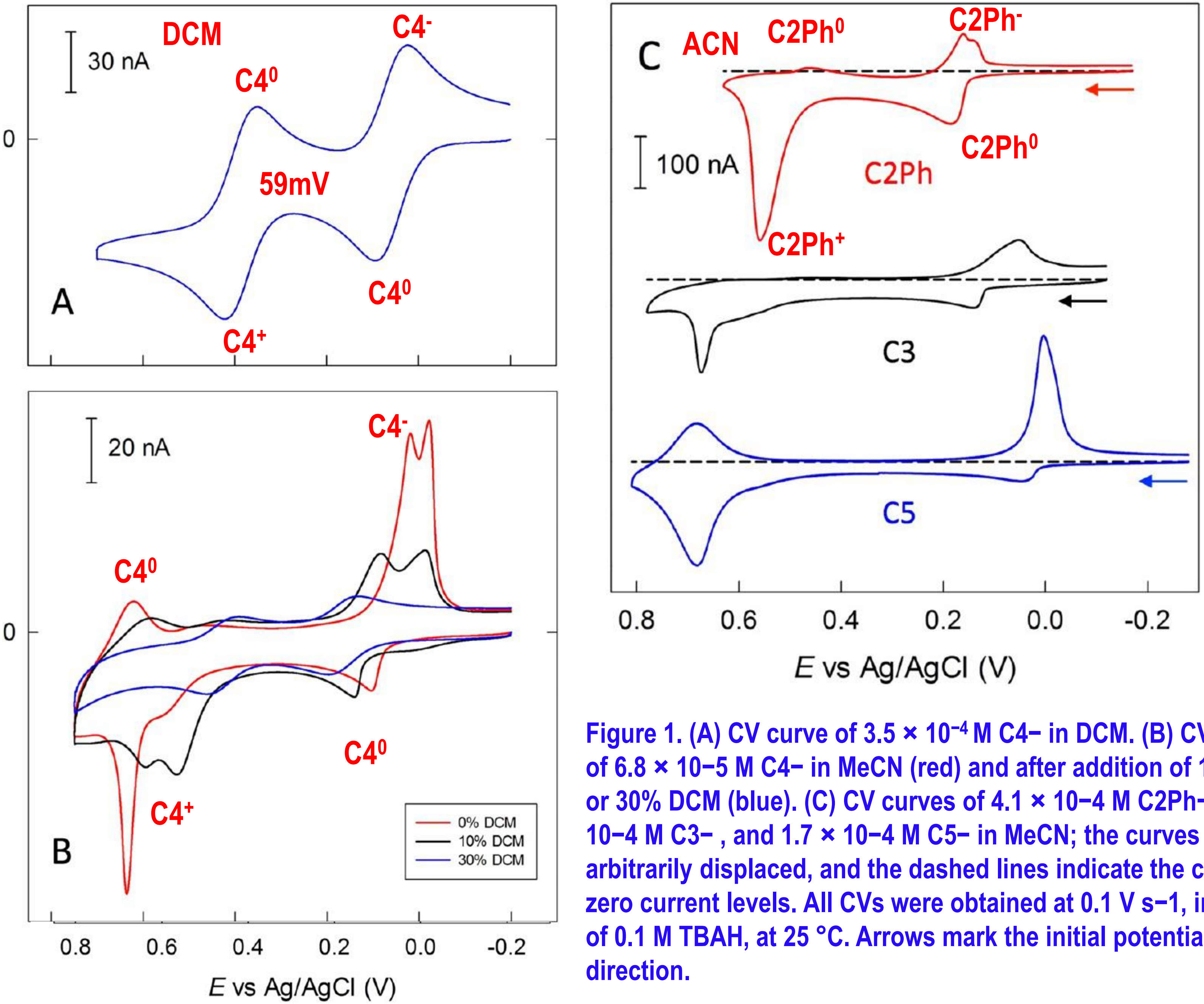
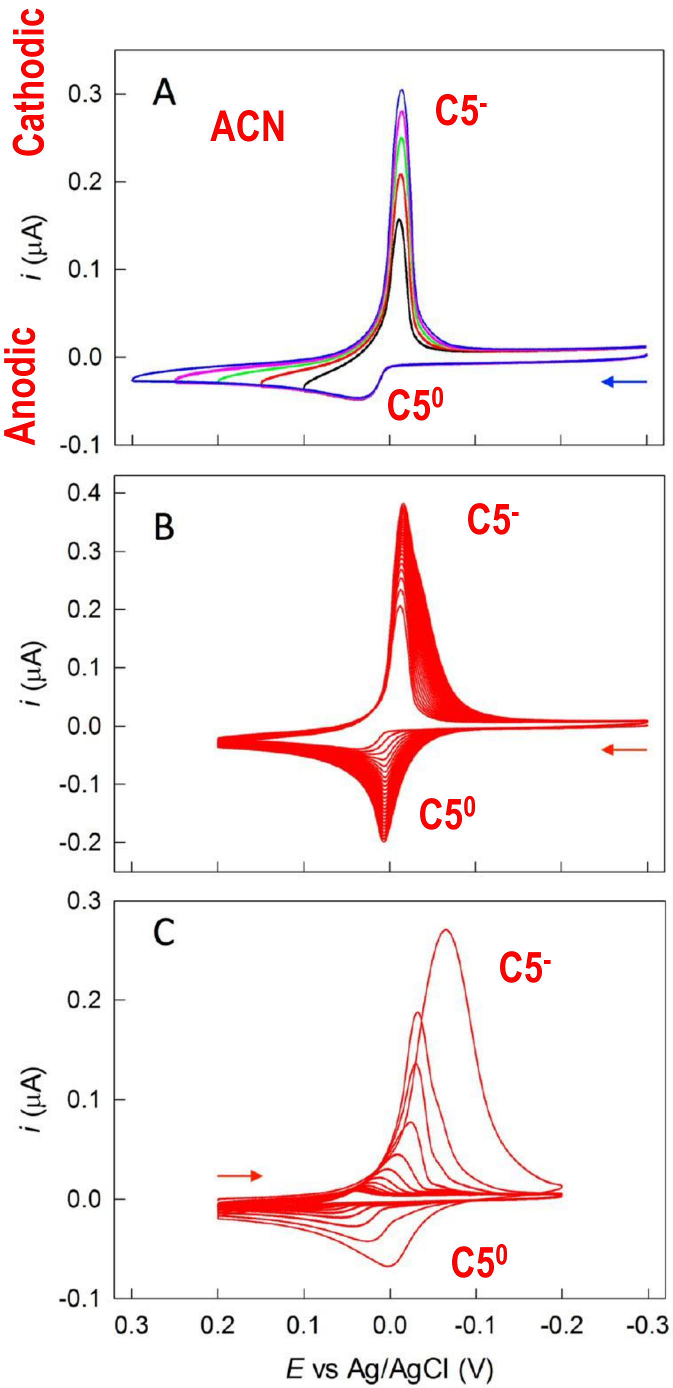


Figure 1. (A) CV curve of 3.5 × 10^{-4} M C4− in DCM. (B) CV curves of 6.8 × 10−5 M C4− in MeCN (red) and after addition of 10 (black) or 30% DCM (blue). (C) CV curves of 4.1 × 10−4 M C2Ph−, 1.4 × 10−4 M C3− , and 1.7 × 10−4 M C5− in MeCN; the curves were arbitrarily displaced, and the dashed lines indicate the corresponding zero current levels. All CVs were obtained at 0.1 V s−1, in the presence of 0.1 M TBAH, at 25 °C. Arrows mark the initial potential-scan direction.

Results and discussion:

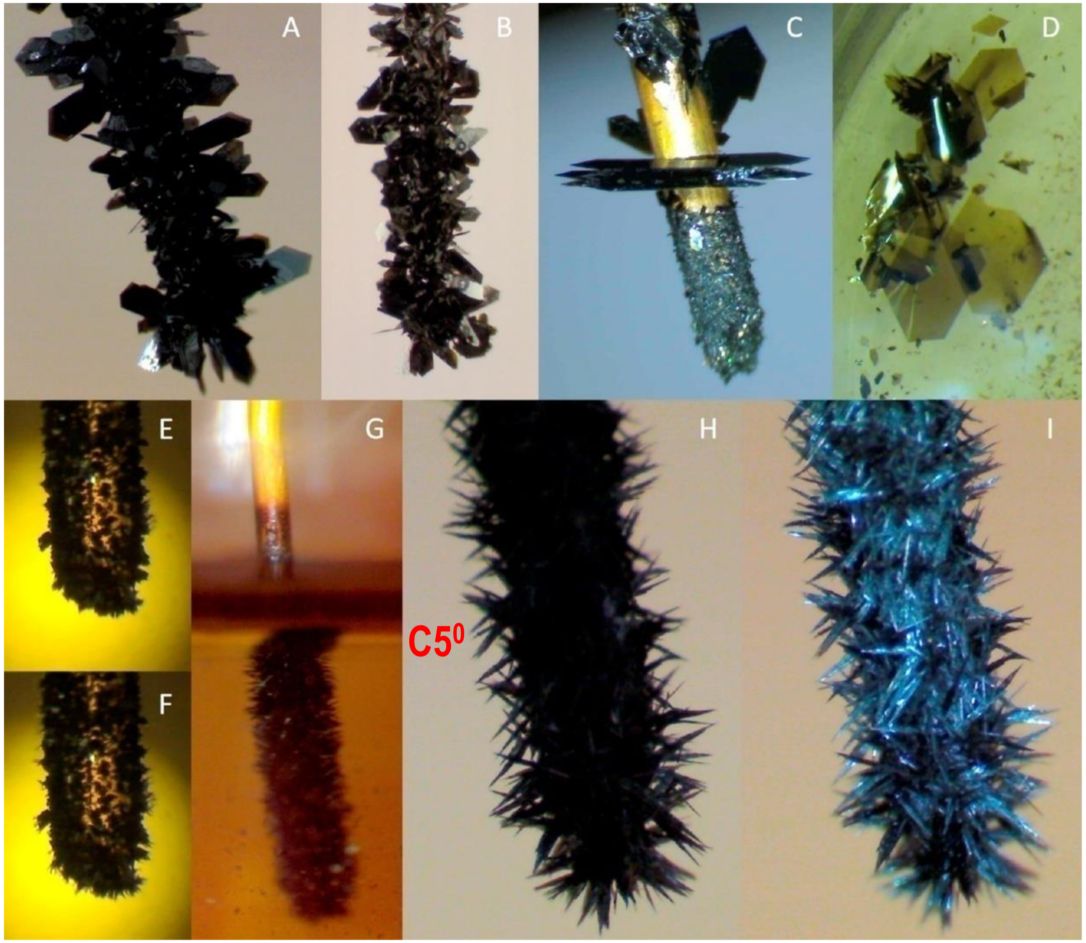


Integration of the first reductive desorption peak yields the charge Q associated with the quantity of cluster deposited and thus the surface coverage $\Gamma = Q/Ae$, where A (in cm^2) is the electrochemical area. surface coverage (Γmono) of 2.72×10^{13} clusters cm^{-2} $monolayer^{-1}$.

Figure 2. CVs of 1.4 × 10−4 M C5− in MeCN/0.1 M TBAH obtained at 0.1 V s−1 and 25 °C. (A) Effect of increasing the reversal potential on the CV of C5−. (B) Multicycle CV of C5−; the initial potential was set to −0.3 V. (C) Multicycle desorption of the C5^{0} deposited in 50 cycles carried out as in plot B; here, the initial potential was set to 0.2V.

Results and discussion:

C4^0



C2Ph^0

Figure 3. (A,B) Crystals of C2Ph^0 covering the gold wire at the end of electrolysis, after extraction of the electrode from the electrochemical cell. (C) Partially uncovered electrode that shows some large crystals of C2Ph^0 . (D) Semitransparent crystals of C2Ph^0 at the bottom of the electrochemical cell. (E,F) Electrode covered by crystals of C4^0, in the electrolytic solution, after 30 and 31 h, respectively. (G) Electrode covered by crystals of C5^0 and still immersed in the electrolytic solution. (H,I) Different contrast images of the same electrode of (G) after extraction from the cell.

Results and discussion:

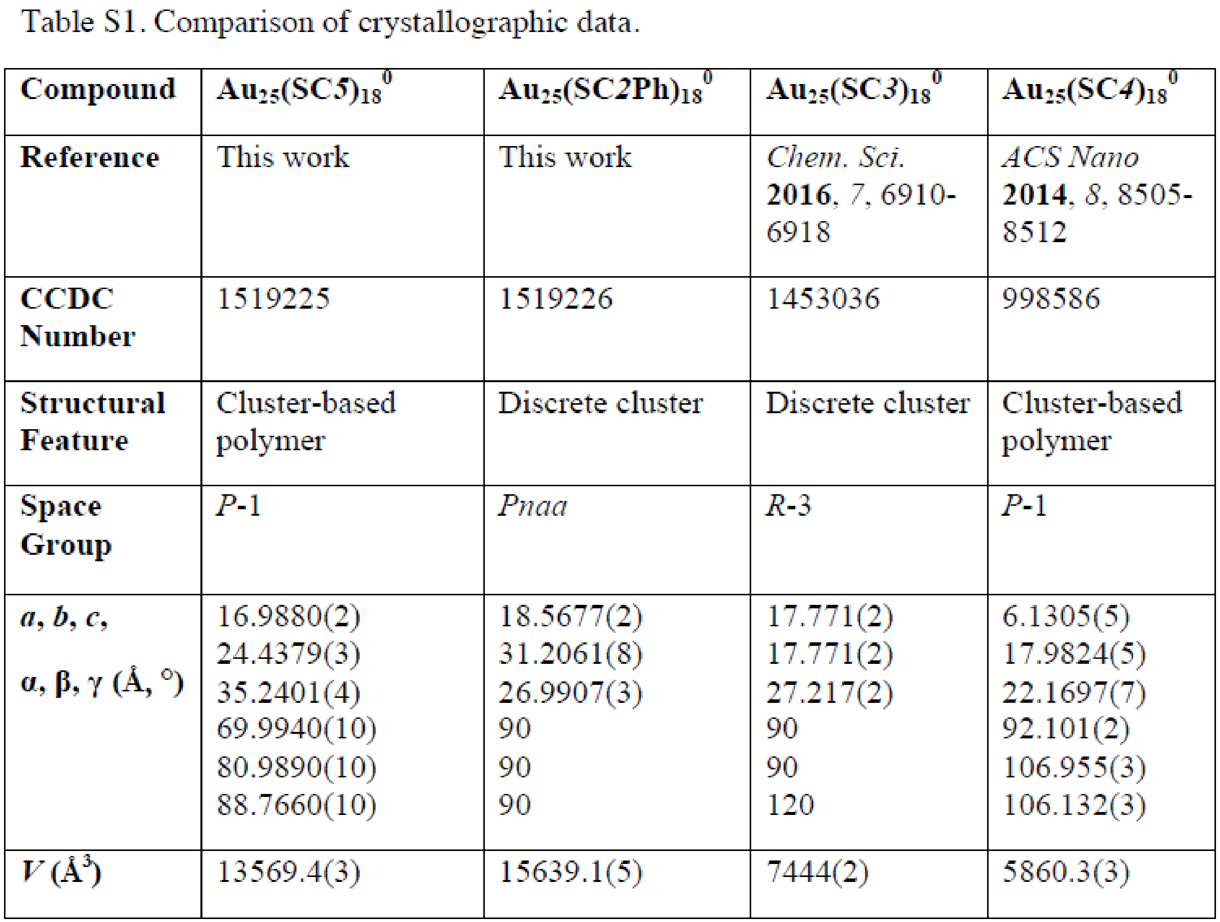
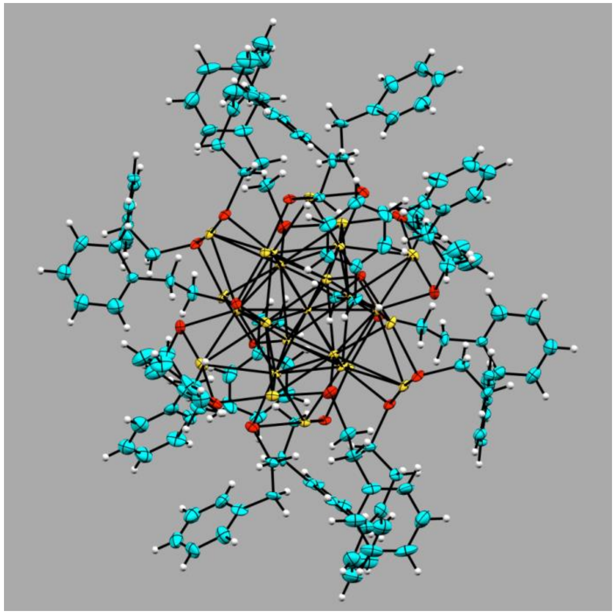


Table S1. Comparison of crystallographic data.

Compound	**$Au_{25}(SC5)_{18}^{0}$**	**$Au_{25}(SC2Ph)_{18}^{0}$**	**$Au_{25}(SC3)_{18}^{0}$**	**$Au_{25}(SC4)_{18}^{0}$**
Reference	This work	This work	*Chem. Sci.* **2016**, *7*, 6910-6918	*ACS Nano* **2014**, *8*, 8505-8512
CCDC Number	1519225	1519226	1453036	998586
Structural Feature	Cluster-based polymer	Discrete cluster	Discrete cluster	Cluster-based polymer
Space Group	*P*-1	*Pnaa*	*R*-3	*P*-1
***a*, *b*, *c*, α, β, γ (Å, °)**	16.9880(2) 24.4379(3) 35.2401(4) 69.9940(10) 80.9890(10) 88.7660(10)	18.5677(2) 31.2061(8) 26.9907(3) 90 90 90	17.771(2) 17.771(2) 27.217(2) 90 90 120	6.1305(5) 17.9824(5) 22.1697(7) 92.101(2) 106.955(3) 106.132(3)
V (Å^3)	13569.4(3)	15639.1(5)	7444(2)	5860.3(3)



Results and discussion:

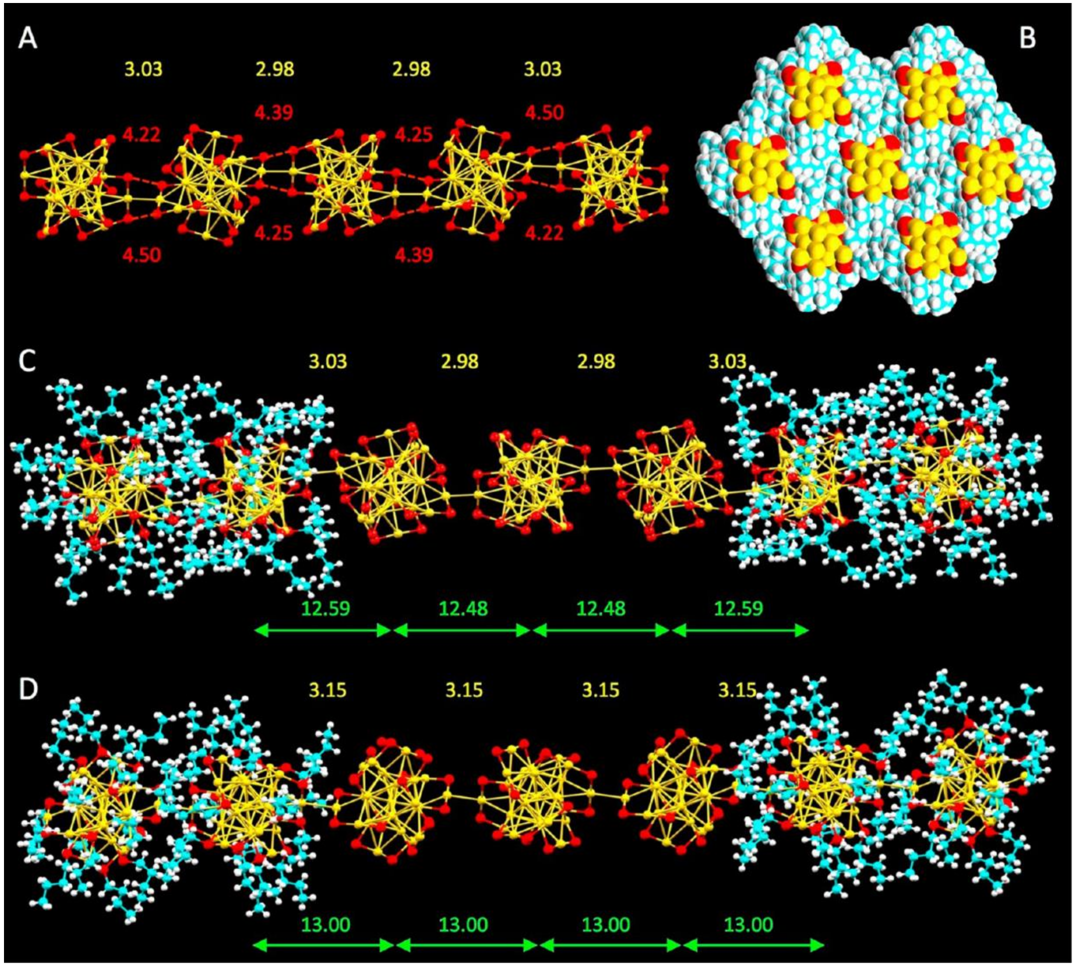


Figure 4. (A) Stick-and-ball view of the $Au_{25}S_{18}$ skeletons of the MPCs found in the $Au_{25}(SC_5)_{18}^0$ crystal, and relevant S−S (red) and bonding Au− Au (yellow) distances. (B) View of the 1D chains along the polymer axis, in space-fill rendering. (C,D) Comparison between the $Au_{25}S_{18}$ skeletons of $Au_{25}(SC_5)_{18}^0$ (C) and $Au_{25}(SC_4)_{18}^0$ (D) with relevant distances (Au−Au bonds in yellow, Au central−Au central in green) between the individual MPCs, where in both (C) and (D), the polymer wires have been partially peeled off (C and H atoms). In all panels, the color codes are Au = yellow, S = red, C = turquoise, and H = white.

Conclusion:

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High quality. High impact.

- Using a properly devised electrocrystallization approach, crystals of thiolate-protected clusters can be prepared in large amount, very high quality, and with a virtually 100% success rate.

- Galvanostatic electrooxidation generates insoluble $Au_{25}(SR)_{18}^0$ clusters that crystallize on the electrode surface and act as tiny electrodes to form a densely packed forest of crystals.

- X-ray crystallographic analysis showed that known structures are easily reproduced.

- The efficiency of the electrocrystallization approach is particularly evident in the improved structural features observed for the long-studied $Au_{25}(SC_2H_4Ph)_{18}^0$.

- This method was tested to prepare the crystals of a new Au_{25} clusters, they made the discovery that the Au_{25} polymerization phenomenon is more general than anticipated.

Future directions:

- If the charge states of clusters are stable and have different solubility then we can crystallize them using electrocrystallization.

Creating high quality crystals in quantity can open doors to following studies:

- Phase transition
- Polymorphism
- High pressure studies (diamond anvil cell)
- Solid state applications


Thank you!