Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORT INFORMATION

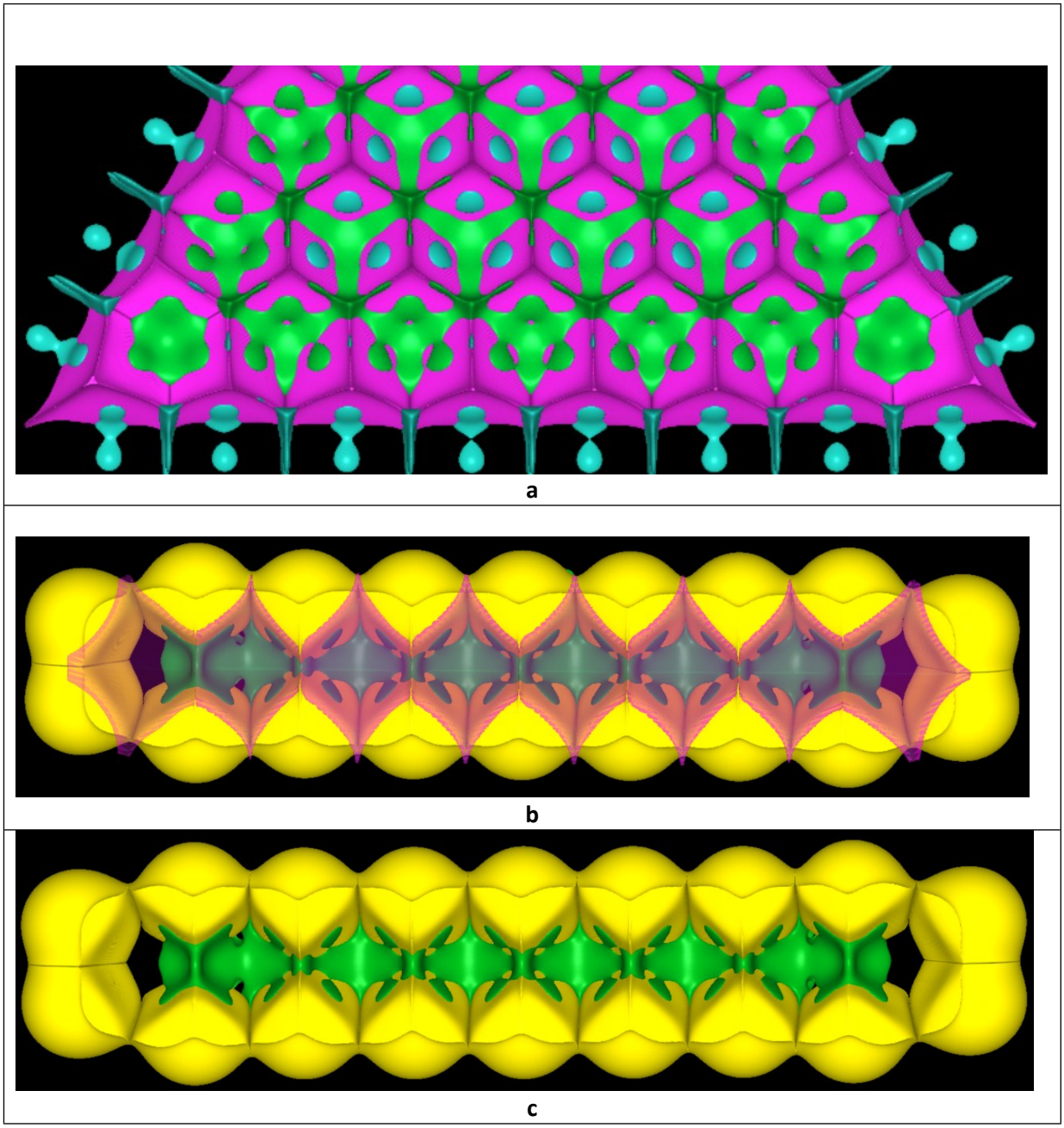
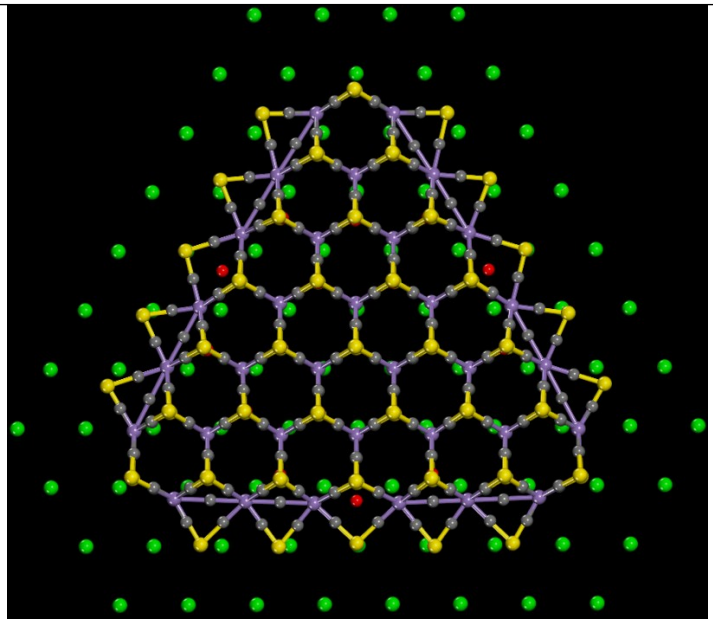


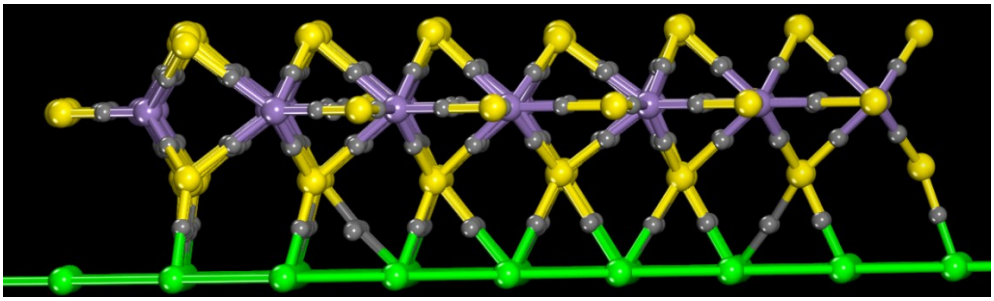
Figure S1. (a) *n8_100S* cluster top-view showing the overlay of the LED = 0.3 au isosurfaces with the atomic basins (pink) of the Mo atoms plane. (b) Side-view including the basins (yellow) of the top and bottom S layers. Some transparency has been applied to the Mo basins. (c) It is clearly seen that the LED=0.3 au isosurface is localized at the border of the Mo basins. Most of the delocalized electrons (LED<0.3 au) are inside the basins of the Mo central plane.

Results for the *n6_50S cluster.*

The optimized geometry and determined graph for the case of the *n6_50S* cluster adsorbed on an Au (111) layer model are shown in Figure S2. Overall, the S atoms of the basal plane adsorb at an average equilibrium distance Re(S-Au) = 2.443 Å. The average topological properties of the S-Au BCPs involving the basal plane S atoms are: ρ_b = 0.0783, the curvatures λ_1 = -0.0711, λ_2 = -0.0677, λ_3 = 0.3458 and $\nabla^2\rho b =$ 0.2071 au. These properties are quite comparable to the corresponding values of the S-Au values for the *n1_100S* cluster supported on Au (111). Figure S3 shows the LED=0.3 au isosurface for this system. It can be seen from the top-view displayed in Fig. S3a that for the top of the *n6_50S* cluster, similar the unsupported *n8_50S* cluster, there are semiconductor LED patterns of separated oblate disks (blue zones) breaking the one-dimensional metallic BRS. This time at the corners and the center of the edges. An identical pattern for the cluster bottom layer can be seen in Figs. S3b and S3c. Note from Fig. S3b that the cluster green zone containing the Mo atoms plane is merged to the Au (111) LED area and extends towards the gold surface. However, in contrast to the *n1_100S* cluster where the S atoms of the basal plane show a metallic arrangement (See Fig. 8c) with the Au111 surface, all the S-Au bonds for the *n6_50S* cluster show the presence of separated oblate disks (yellow disks) around the BCPs, suggesting the semiconductor LED pattern of these sites.



a



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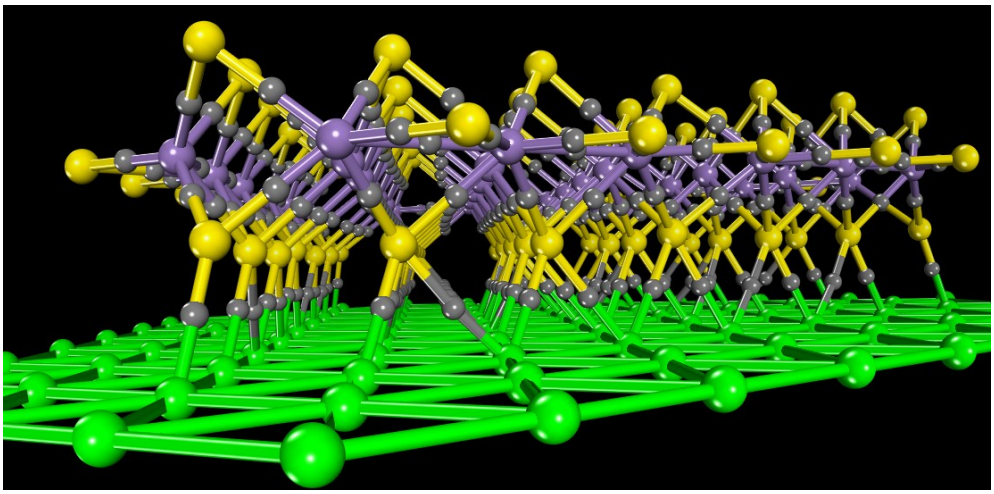
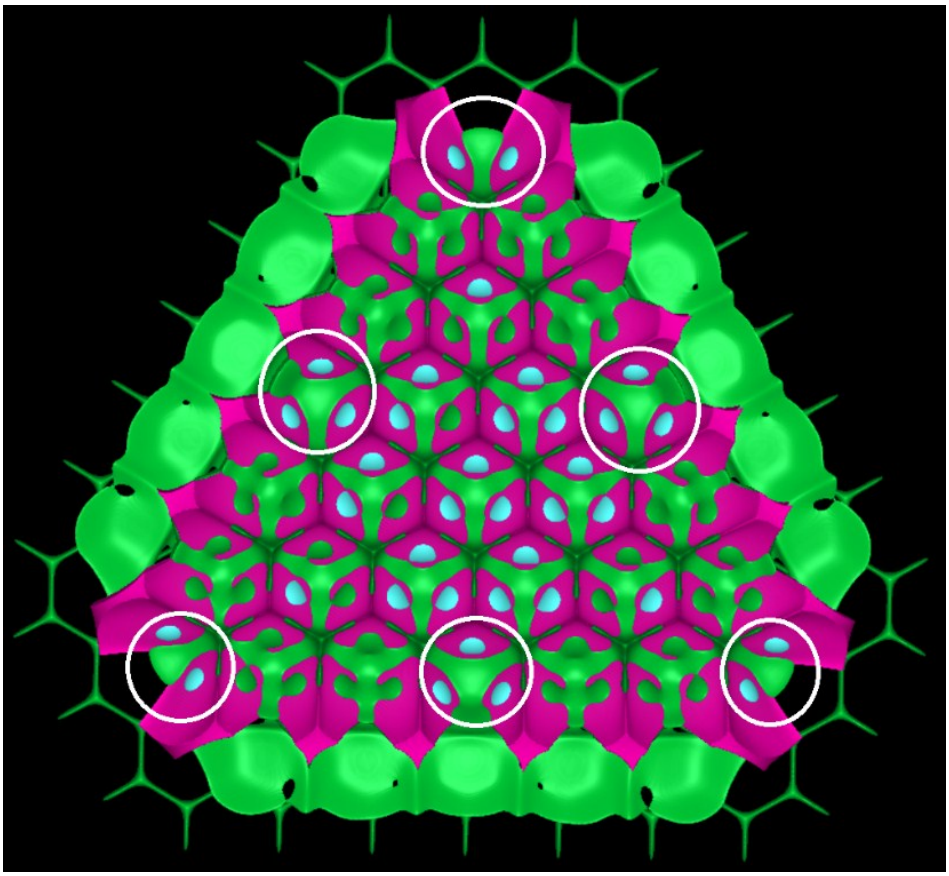
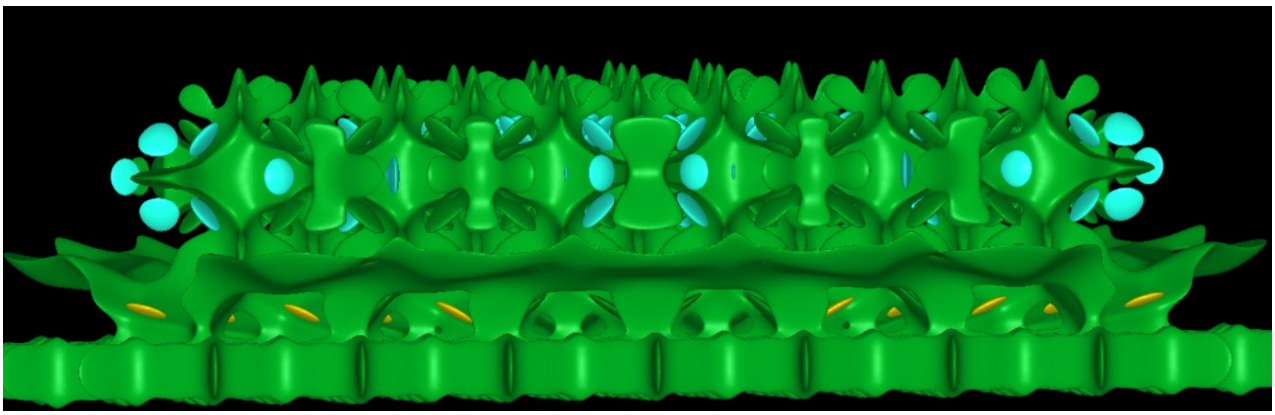


c

Figure S2. Top-view (a) and side-view (b) and (c) of the optimized geometry of the *n6_50S* cluster supported on an Au (111) layer model. Pink, yellow and green spheres denote the Mo, S and Au atoms, respectively. Gray and red (in a) spheres denote bond and cage CPs.



a



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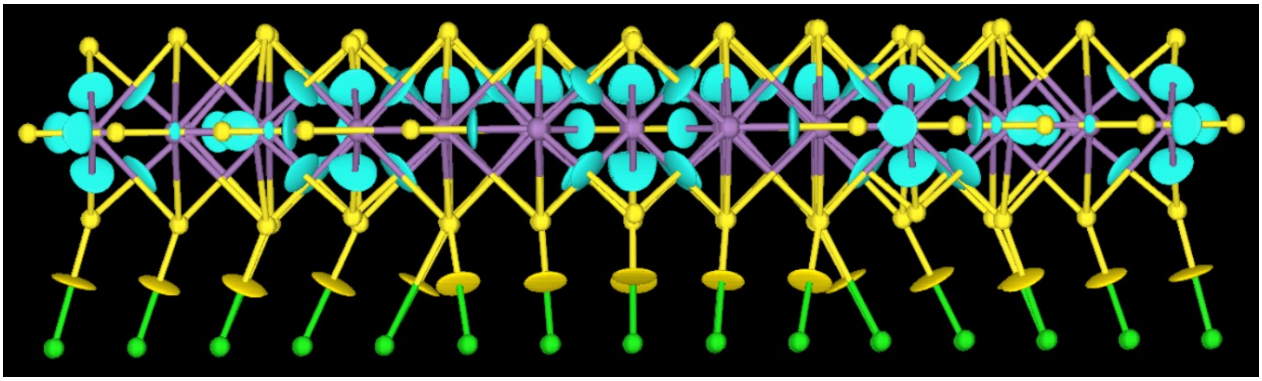

c

Figure S3. Top-view (a) and side-view (b) of the LED isosurface with a value of 0.3 au showing the region of most delocalized electrons for the *n6_100S* cluster supported on an Au (111) surface model. (a) Like the *n8_50S* cluster (Fig. 6), most of the zones of highly electron delocalization around the BCPs (blue zones) are localized in separates regions of the space showing a semiconductor pattern. White circles highlight the fact that at the edges, the one-dimensional metallic ring is broken. (b) The cluster green zone containing the Mo atoms plane is merged to the Au (111) LED area and extends towards the gold surface. (c) The green zone has been removed to highlight that almost all BCPs are in separated like-disk areas (blue and yellow for Mo-S and S-Au bonds, respectively). Pink, yellow and green spheres denote the Mo, S and Au atoms, respectively.