Electrochemical active surface area was measured according to anodic oxidation of chemisorbed iodine (Rodriguez J.F. et al., J Electroanal. Chem., 233 (1987) 283). The total quantity of chemisorbed iodine is directly proportional to the charge for anodic oxidation of adsorbed iodine to aqueous IO$_3^-$ (peak in the range from 1.4 to 1.6 V shown in the dotted curve above). The equation is $\text{I}_{\text{ads}} + 3 \text{H}_2\text{O} = \text{IO}_3^{-} (\text{aq}) + 6 \text{H}^{+} (\text{aq}) + 5\text{e}^{-}$. The gold surface area is related to this anodic charge according to this equation $A = (Q - Q_{c})_{\text{ox,1}} / 5FC_{\text{I,calc}}$, where $(Q - Q_{c})_{\text{ox,1}}$ is corrected oxidative charge, $F$ Faraday’s constant and $C_{\text{I,calc}}$ the calculated iodine packing density. If we assume hexagonal close-packing of chemisorbed iodine, the obtained $C_{\text{I,calc}}$ is 1.04 nmol/cm$^2$. Cyclic voltammogram for the clean Au surface with 20 mm$^2$ was detected in 1 M H$_2$SO$_4$. Then, same size Au surface after been immersed in 1 M KI solution for 30 min was run in the same solution. The charge difference between clean Au surface and the surface with KI in the potential range from 1.4 to 1.6 V is about 15 $\mu$C, which leads to the active surface coverage is only 3 mm$^2$. 
$^{13}$C NMR spectra for pure WOC Mn$_4$O$_4$(Ph$_2$PO$_2$)$_6$ (a), 4-ido phenyl phenyl phosphonic acid (IPPA) (b) and ligand exchange reaction product between Mn$_4$O$_4$(Ph$_2$PO$_2$)$_6$ and IPPA (c). Obviously, after mixing Mn$_4$O$_4$(Ph$_2$PO$_2$)$_6$ with IPPA together, there is a new peak at 142 ppm shown up compared to the $^{13}$C NMR spectra of pure Mn$_4$O$_4$(Ph$_2$PO$_2$)$_6$ and IPPA, which indicates ligand exchange reaction happens according to the way below.
Effect of the concentration of IPPA used for immersing on the amount of iodine attached to Au surfaces. The data were obtained from the quantification of XPS data. It is estimated from the $(I3d_{3/2} + I3d_{3/2}) \times RSF_{Au} / [(Au4f_{5/2} + Au4f_{7/2}) \times RSF_I]$ ratio of the integrated signals. It is obvious that with the increase of immersed concentration of IPPA, the amount of iodine on the surface of Au rises greatly at the beginning. With further increase of the immersed concentration of IPPA, the increase extent for the amount of iodine on the surface of Au decreases.
AFM images and particle analysis of Au surfaces immersed in IPPA solutions of different concentrations at 2×2 µm magnification: (a) and (e) 0 (clean Au control), (b) and (f) 26 µM, (c) and (g) 0.35 mM and (d) and (h) 10 mM. AFM analysis of films was done using a Digital Instruments Multimode Nanoscope IIIa SPM equipped with phosphorus doped Si tips (Multi75 Metrology Probes, Veeco; resonant frequency, 300 kHz; spring constant, 40 N/m) in tapping mode.

AFM data (Supporting Information) shows the clean Au surface exhibits a uniform texture with grains having a particle depth distribution in the range of 2.1 to 10 nm (most probable 6.0 nm). After forming a chemisorbed monolayer of IPPA on the Au surface (by soaking in 26 µM IPPA solution according to the XPS data), the surface texture becomes coarser and the grain size becomes larger. The
particle depth distribution increases (most probable height 7.7 nm) and broadens, from 2.1 to 15.4 nm, compared to that of the control. AFM reveals that adsorption of additional IPPA from more concentration solutions which forms new interactions according to XPS, further increases the particle depth distribution, particle height, and changes the distribution from a single Gaussian to an asymmetric distribution indicative of two or more populations of particle sizes (Supporting Information). This asymmetric distribution demonstrates that formation of a second or multilayer occurs above the first self-assembly layer.

Although an experimental measure of the molecular length for IPPA is not known, the theoretical height can be accurately estimated to be 10 Å from the I atom to one of the O atoms. This distance would correspond to the possible depth along the surface normal assuming a vertical orientation of the IPPA molecule. According to the AFM data, the chemisorbed IPPA layer results in a 1.7 nm increase of particle height. For the Au surface after soaking in 0.35 mM and 10 mM IPPA solution, respectively, corresponding to IPPA concentrations for which XPS data shows the formation of an additional physisorbed IPPA layer, adsorption from 0.35 mM IPPA in solution gives a distribution of particle depths ranging from 2.1 to 26.0 nm, that is 1.6-fold broader than for the sample soaked in 26 µM IPPA solution, and a most probable particle height of 13.8 nm. Adsorption from 10 mM IPPA solution further increases the particle depth distribution and particle height, while also changing the distribution from a single Gaussian to an asymmetric distribution indicative of two or more populations of particle sizes. Additionally, there are particles as small as 10.0 nm on the surface, but the population is dominated by larger sizes that peak at 15.5 nm and drop off in size almost linearly rather than by a normal distribution. This asymmetric distribution demonstrates that formation of a second or multilayer occurs above the first self-assembly layer. Also, this outer layer is not subject to the same uniform forces that build the chemisorbed layer, but rather reflect more random physical sources.
AFM image (a) and particle depth distribution (b) for the Au surface after having been soaked in 0.35 mM IPPA solution and then sonicated for five cycles. Compared to the original image without sonication, the particle grains become more distinct since some small particles between grains are removed by sonication. The particle depth distribution greatly shifts to lower depth upon sonication, from 2.1 nm to 21 nm, with most of particles having a height of 8.0 nm. This is 2.0 nm bigger than that for the clean Au surface, which we attribute to the presence of a chemisorbed IPPA monolayer. The distribution of the depth profile is not symmetric; there is a tail extending to high depths, but not so wide a distribution as prior to sonication. The XPS data allow us to rule out the presence of physisorbed IPPA following sonication. Hence, we are uncertain of the source of the asymmetry in the particle depth distribution following sonication.
Cyclic voltammograms for clean Au electrode in 0.3 mM IPPA of 0.1 M KCl solution (a) and in blank 0.1 M KCl solution (b) with the scan rate of 50 mV/s. It is obvious that there are two broad peaks located at -0.35 V and 0.5 V respectively in the system with IPPA. The one at -0.35 V reflects the formation of an ordered iodide adlayer. The other one is attributed to the iodide induced lifting of the reconstruction of Au surface.
XPS spectra for I\textit{3d} on the multiple sonicated surface of Au after electrochemistry measurement (a) and on the same Au surface only after multiple sonication (b). It can be seen that after CV is run in the range of -0.6 ~ 0 V, the self-assembled IPPA monolayer is almost gone from the surface since the intensity for the peak of I\textit{3d} decreases greatly after EC detection, which confirms that the ordered adlayer goes into solution at the potential of -0.35 V.
XPS survey spectrum for Au surface with WOC Mn$_4$O$_4$(Ph$_2$PO$_2$)$_6$ through ligand exchange reaction with IPPA. The immersed concentration of Mn$_4$O$_4$(Ph$_2$PO$_2$)$_6$ is 0.25 mM. This spectrum is similar to that of Au surface only with IPPA. However, there are few slight differences. The one is that the peak intensity attributed to the iodine element from IPPA decreases a little. The other one is a little increase of the intensity of the shoulder peak located at 642.5 eV. It is related to the appearance of Mn complex Mn$_4$O$_4$(Ph$_2$PO$_2$)$_6$. Anyway, for the characterization of Mn$_4$O$_4$(Ph$_2$PO$_2$)$_6$ with XPS survey technique, there is no distinct binding peak shown in the survey spectrum for claiming the existence of WOC Mn$_4$O$_4$(Ph$_2$PO$_2$)$_6$. It is because the small amount of Mn$_4$O$_4$(Ph$_2$PO$_2$)$_6$ on Au surface causes overlapping of its characteristic binding energy peak for P$_2$p$_{3/2}$ by strong background peak corresponding to the binding energy for Au4f and that for Mn2p$_{3/2}$ by relevant strong peak consistent with Au4p.
XPS spectra of Mn2p and Au4p for the Au surface: (a) coated with IPPA, then immersed in 0.25 mM Mn₄O₄(Ph₂PO₂)₆ solution for 24 h, and finally sonicated, (b) directly immersed in 0.3 mM Mn₄O₄(Ph₂PO₂)₆ solution for 24 h. The characteristic peak corresponding to Mn2p₁/₂ is still on the surface of Au with IPPA but there is no Mn2p₁/₂ peak at all for the sample without IPPA as a bridge. It is obvious that IPPA on the surface of Au has a important role for the attachment of WOC Mn₄O₄(Ph₂PO₂)₆ onto Au surface since without IPPA, Mn₄O₄(Ph₂PO₂)₆ can be attached onto Au surface at all even without sonication.