Supplementary Information.
(A.W. Snow, E.E. Foos, M.M Coble, M.G. Ancona and G.G. Jernigan, "Fluorine-Labeling as a Diagnostic for Thiol-Ligand and Gold Nanocluster Self-Assembly")

IR and NMR spectra of the free oxyethylene thiol ligands, **1** and **2**, and of the fluorine-labeled cluster are depicted in Figs. S1 and S2 respectively for individual and comparative purposes.

In the infrared spectrum the fluorine-terminated oxyethylene thiol, **1**, displays bands that correlate with its functional groups: monofluoroalkyl C-F stretching (1045 cm^{-1}), the weak thiol S-H stretching (2555 cm^{-1}), and other bands associated with an amorphous oxyethylene oligomer moiety (CH_2 stretching, 3000-2700 cm^{-1}; CH_2 scissoring and wagging, 1500-1200 cm^{-1}; the C-O stretching, 1150-1050 cm^{-1}; and various weaker C-O stretching and CH_2 rocking modes, 1000-700 cm^{-1}). This oxyethylene oligomer pattern is very similar to that observed for the methoxy terminated oxyethylene thiol, **2**, and has been long observed for molten poly(ethylene glycol).[1] The spectrum of the of the oxyethylene thiol mixture of **1** and **2** on the gold cluster is depicted in Fig. S1. With the exception of the disappearance of the weak S-H stretching of the free thiols, this spectrum is additive of these two thiols although the C-H stretching bands are less intense.

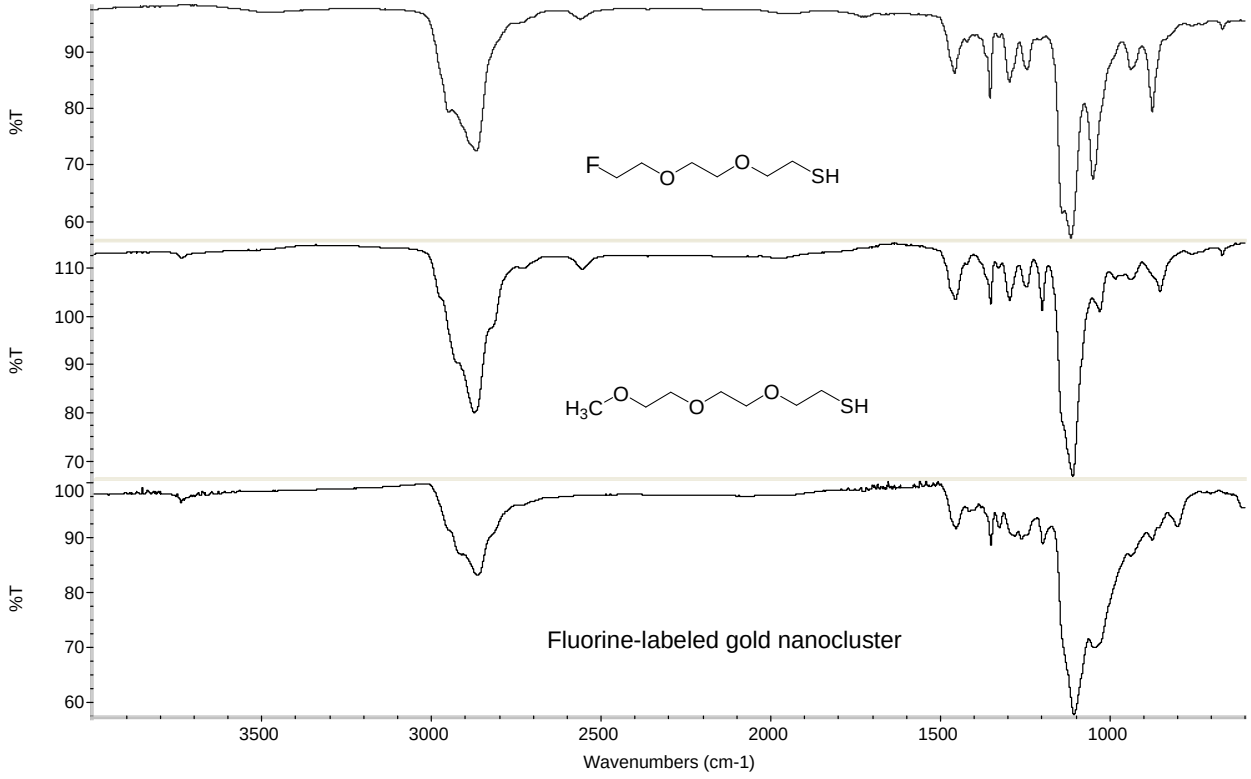

Fig. S1. IR spectra of the fluorine labeled oxyethylene thiol (**1**), of the methoxy terminated analog (**2**) and of the gold cluster stabilized by the mixture of the two thiols.

The ^{1}H and ^{19}F NMR spectra are depicted in Fig. S2. The chemical shifts vertically aligned for comparison of the free thiol ligand resonances with those bound to the gold nanocluster. The proton resonances for the free fluorine-terminated thiol ligand, **1**, are narrow with well-defined hyperfine splitting. In addition to the S-H triplet at 1.52 ppm (not shown) are resonances from the protons α to the thiol group at 2.63 ppm (doublet of triplets) and from the $-CH_2F$ terminal group at 4.54 ppm (doublet of triplets) are completely resolved. The geminal fluorine splitting of this resonance is particularly distinctive. The oxyethylene proton resonance at 3.5-3.8 overlap, but the hyperfine structure is resolved. Likewise, resonances from the methoxy terminated oxyethylene thiol, **2**, consist of the S-H triplet at 1.51 ppm (not shown), the protons α to the thiol group at 2.41 ppm (doublet of triplets), the terminal methoxy group at 3.30 ppm (singlet) and the remaining oxyethylene protons at 3.45-3.60 ppm. When these ligands are bonded to the gold nanocluster surface, the hyperfine structure is lost, and their resonances are considerably broadened with those closest to the bonded sulfur being the most broadened. In the 1H NMR spectrum of the nanocluster the ligand proton resonances appear at chemical shifts corresponding to those of the free thiol ligands with the $-CH_2F$ and $-OCH_3$ terminal groups being the least broadened and the CH_2 α to the sulfur being broadening beyond detection. The ^{19}F NMR spectra of the free ligand **1** and the cluster analogously display a well resolved free ligand resonance at -223.30 ppm with hyperfine structure a signature of the $-CH_2CH_2F$ group (triplet of triplets)[2] that becomes on attachment to the gold nanocluster a featureless broadening signal at a very slightly different chemical shift (-222.6 ppm).

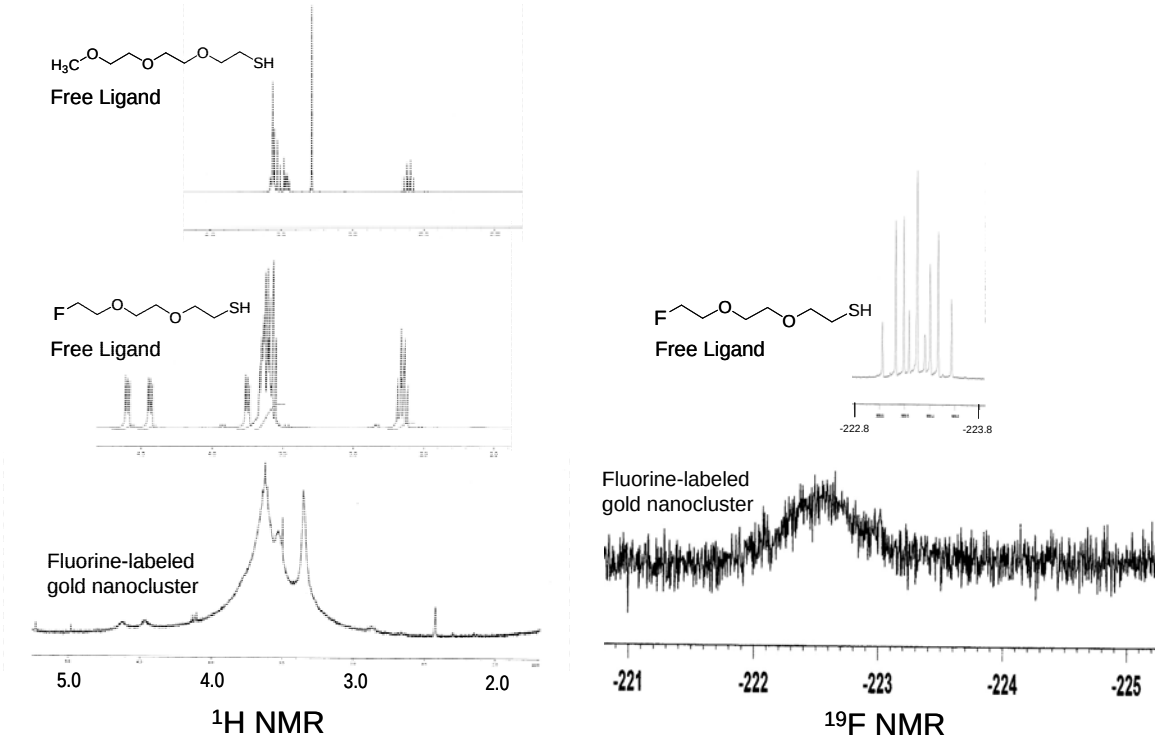

Fig. S2. ^{1}H and ^{19}F NMR spectra of the fluorine labeled oxyethylene thiol (**1**), of the methoxy terminated analog (**2**) and of the gold cluster stabilized by the mixture of the two thiols ligands.

References.

1. (a) Davison, W. H. T. *J. Chem. Soc*. **1955**, 3270, (b) Matsuura, H.; Miyazawa, T. *J. Poly. Sci. A-2*, **1969**, *7*, 1735.

2. Mooney, E. F. *An Introduction to 19F NMR Spectroscopy*, Heyden & Son, Inc.: London, 1970; p. 70.