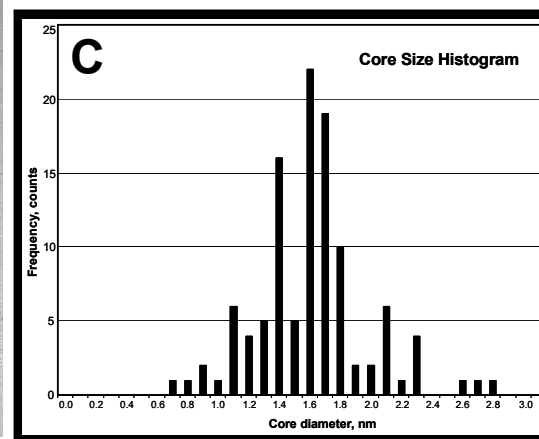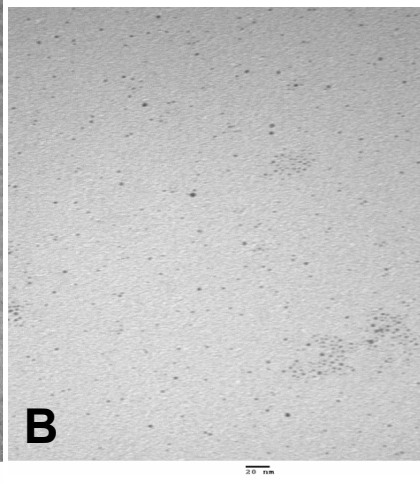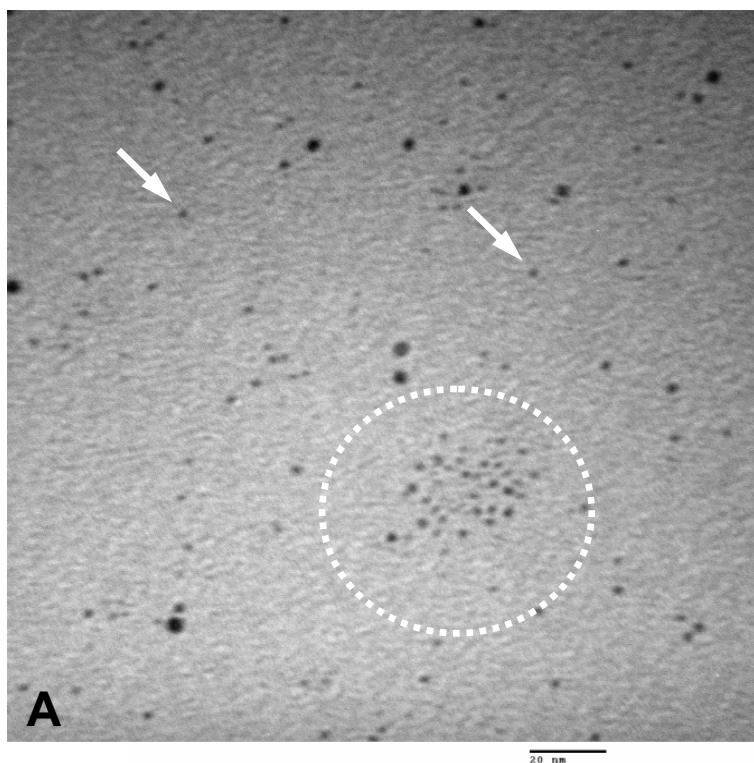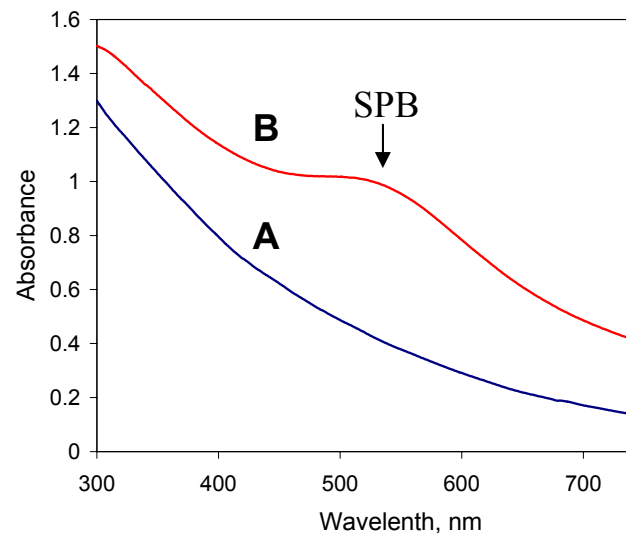# Supporting Materials
"Covalently Networked Monolayer Protected Nanoparticle Films"

D.J. Tognarelli, Robert B. Miller, Rebecca Pompano, Andrew Loftus, Daniel Sheibley and Michael C. Leopold*
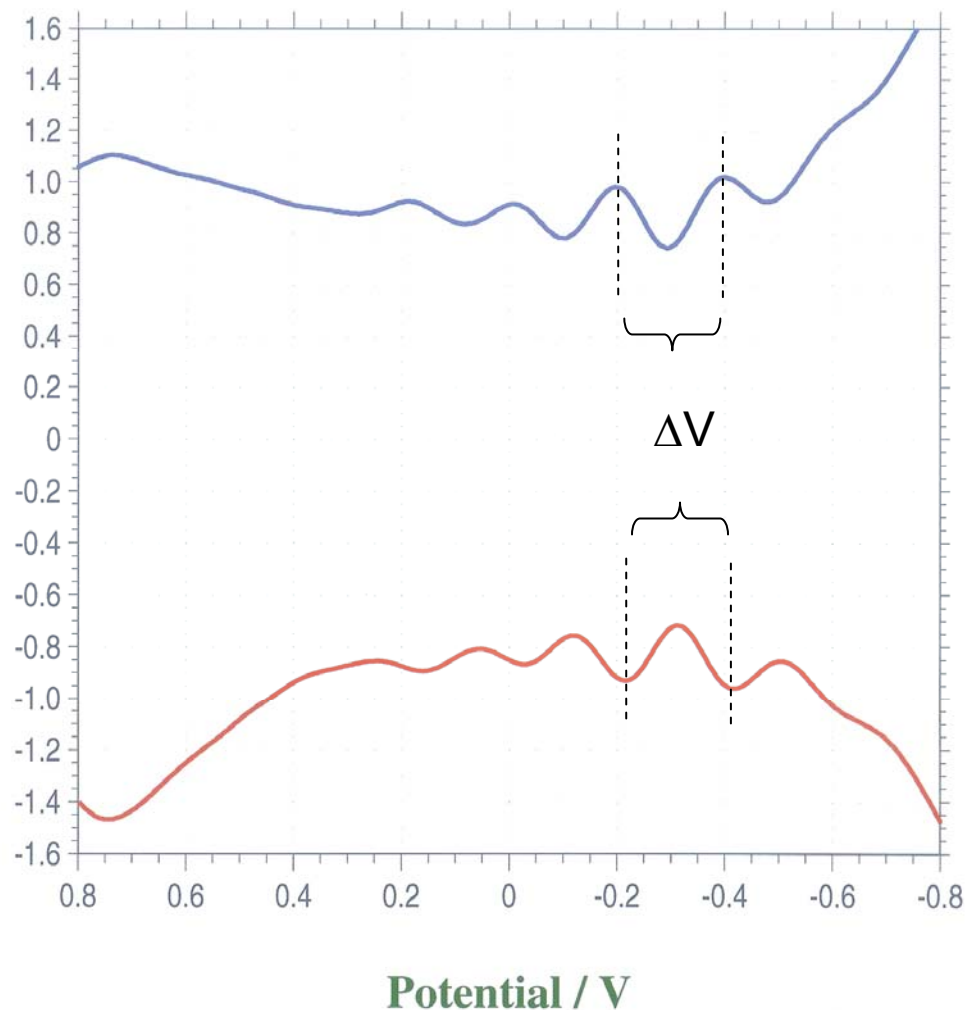Department of Chemistry, Gottwald Science Center, University of Richmond, Richmond, Virginia, 23173, USA.

Figure SM-0 (right). Typical UV-Vis spectra of hexanethiolate (C6) MPC with an _average composition_ of $Au_{140}(C6)_{53}$ in solution (A) and assembled into a film after modification (B). Spectra for MPC films usually display a surface plasmon band (SPB) at ~520 nm, a result of the MPCs being connected in close proximity within the film. UV-Vis spectra of MPC films are typically very similar regardless of how the nanoparticles are networked together.
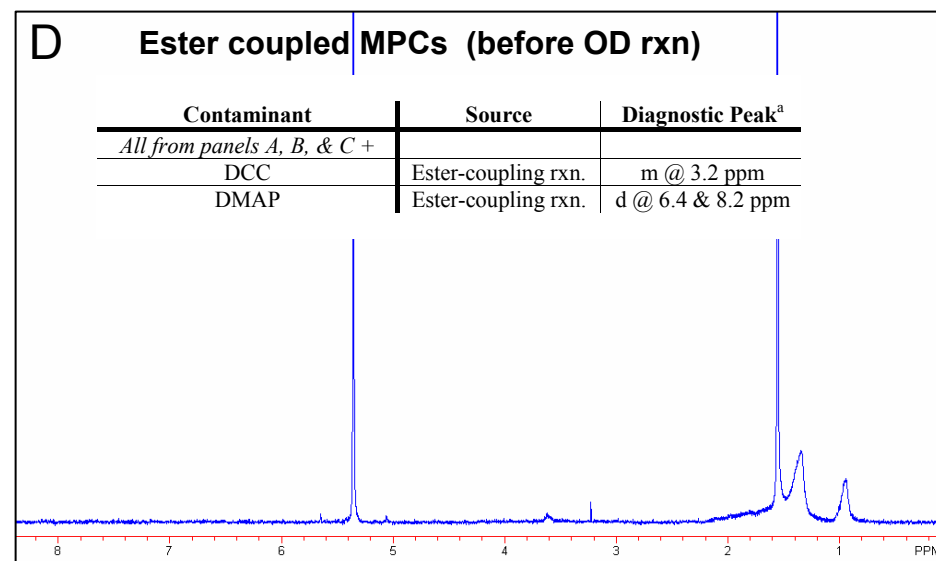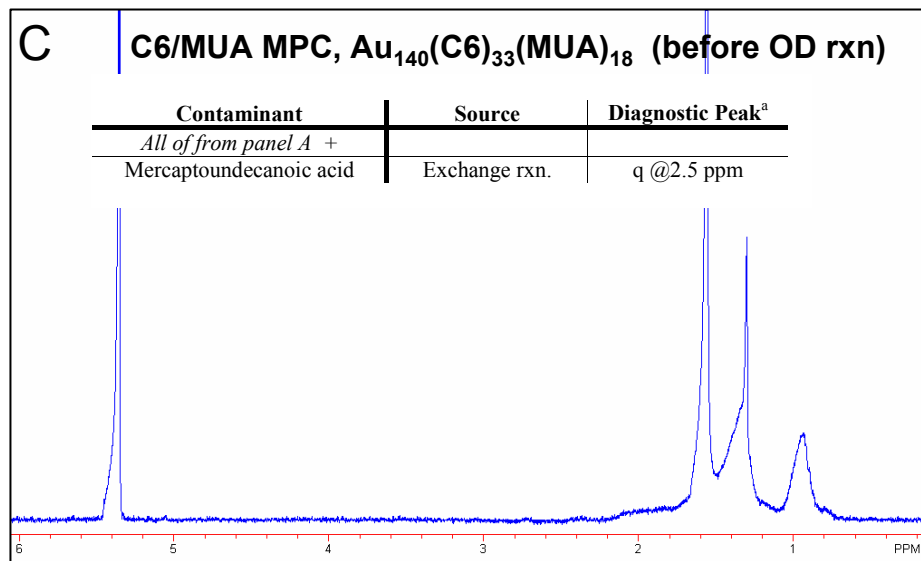

Figure SM-1 (above). Representative transmission electron microscopy analysis of C6 MPC starting material at (A) 250,000x and (B) 100, magnification. Measurement bars at the bottom right of each image are 20 nm. The images serve to show the presence of both a polydispersity in sizes and a predominant population of cores that are approximately 2 nm in size (examples with arrows and circled). These images are similar to found in the literature[26] of other MPCs with core diameters of ~1.5 nm. (C) Histogram of core sizes for the image in A showing the high frequen nanoparticles with 1.6-1.7 core diameters (average = $1.6_6 \pm 0.4_9$ nm; count = 113).

Figure SM-2. Typical anodic (lower) and cathodic (upper) differential pulse voltammetry (DPV) scans showing the quantized double layer (QDL) charging for the C6 MPC starting material in solution of CH_2Cl_2 with tetrabuylammonium perchlorate (TBAP, 0.1 M) as a supporting electrolyte. By measuring peak spacing (ΔV), DPV can be used to determine the average core size of nanoparticles. For this study, the average peak spacing, 0.255 ($\pm$0.035) V corresponds to nanoparticles with a capacitance of 0.66 ($\pm$0.12) aF. These results correlate with literature reports[34-35] where similar measurements of peak spacing/capacitance and corresponding TEM imaging were representative of MPCs with an average core size of 1.6 ($\pm$0.1$_5$) nm.

A C6 MPC, $Au_{140}(C6)_{53}$ (before OD rxn)

Contaminant	Source	Diagnostic Peak[a]
Hexanethiol	MPC synthesis	q @ 2.5 ppm
Disulfide	MPC synthesis	t @ 2.7 ppm
Tetraoctylammonium bromide	MPC synthesis	t @ 3.3-3.4 ppm

B C6/MUD MPC, $Au_{140}(C6)_{33}(MUD)_{20}$ (before OD rxn)

Contaminant	Source	Diagnostic Peak[a]
All of from panel A +		
Mercaptoundecanol	Exchange rxn.	q @ 2.5 ppm

C C6/MUA MPC, $Au_{140}(C6)_{33}(MUA)_{18}$ (before OD rxn)

Contaminant	Source	Diagnostic Peak[a]
All of from panel A +		
Mercaptoundecanoic acid	Exchange rxn.	q @2.5 ppm

D Ester coupled MPCs (before OD rxn)

| Contaminant	Source	Diagnostic Peak[a]
All from panels A, B, & C +		
DCC	Ester-coupling rxn.	m @ 3.2 ppm
DMAP	Ester-coupling rxn.	d @ 6.4 & 8.2 ppm

Figure SM-3. ^{1}H NMR spectra of MPCs <u>before</u> oxidative decomposition (OD) with iodine: (A) the starting C6 MPCs, (B) the C6/MUD exchanged MPCs, (C) the C6/MUA exchanged MPCs, and (D) the material after ester coupling. The relatively featureless spectra are expectedly broadened and show the presence of only very trace amounts, if any, of contamination. The specific diagnostic peaks for potential contaminants are listed in the table of each panel.

[a] Diagnostic peaks for contaminants determined by independent NMR spectra of these materials (not shown).
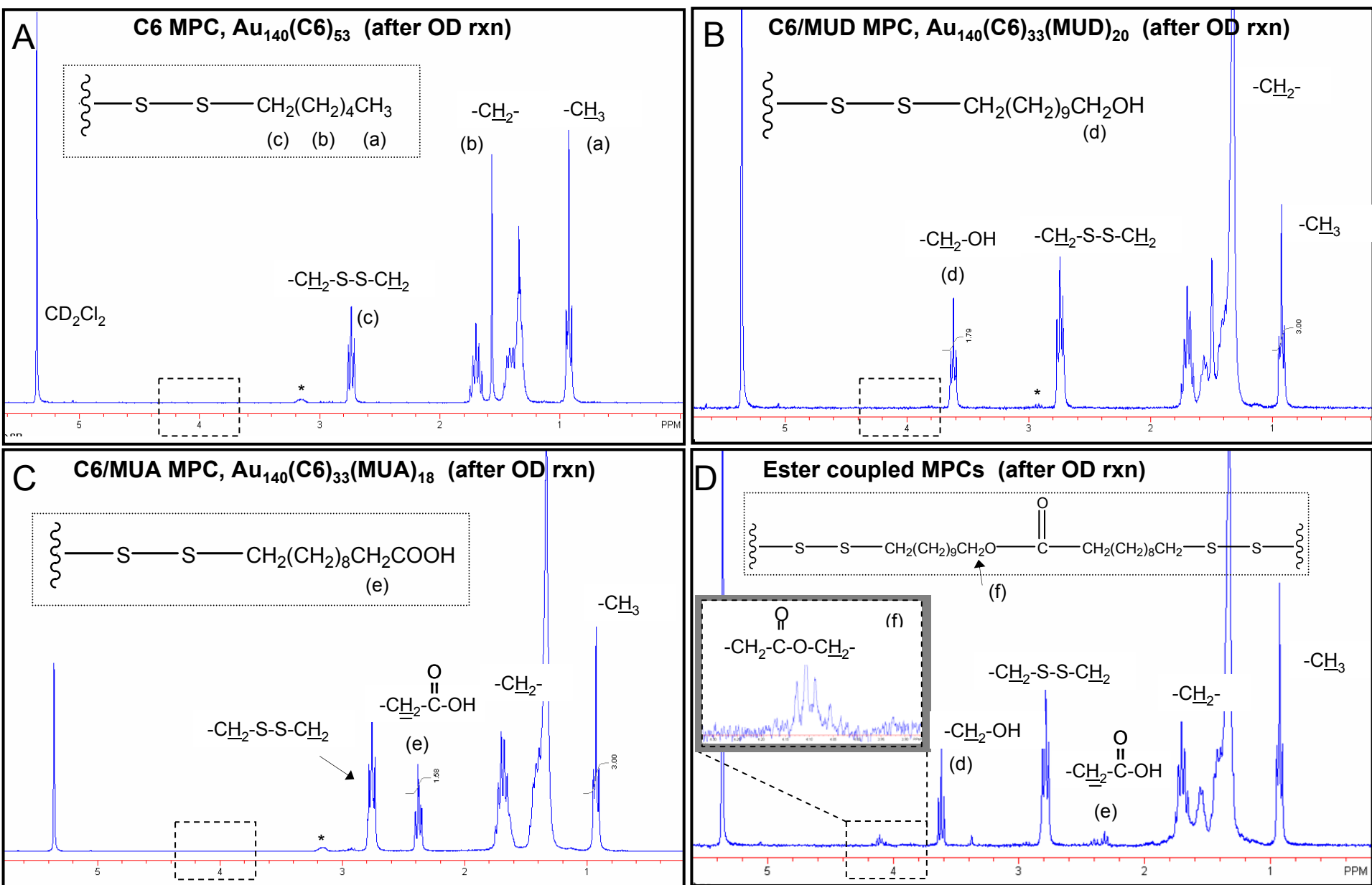
Figure SM-4. ¹H NMR spectra of MPCs <u>after</u> oxidative decomposition (OD) with iodine: (A) the starting C6 MPCs, (B) the C6/MUD exchanged MPCs, (C) the C6/MUA exchanged MPCs, and (D) the material after ester coupling. Spectral assignments of ¹H chemical shifts: methyl (a), methylene (b), disulfide (c), methylene with hydroxyl group (d), methylene with carboxylic acid group (e), and methylene with ester group (f). Spectral location of esters is defined in each panel (- - -) and explained as an inset in D to show the triplet resulting from the presence of the ester. The signal is expectedly low considering it is likely only a small amount of OH and COOH groups will be optimal for coupling. Note: * indicates residual material from MPC synthesis (tetraoctylammonium bromide) or ester coupling reaction (DMAP and DCC).
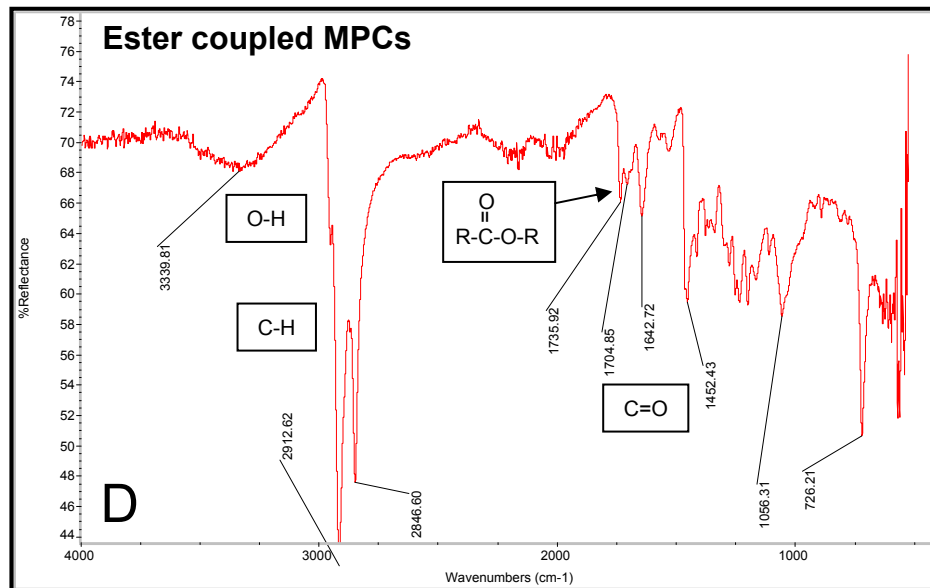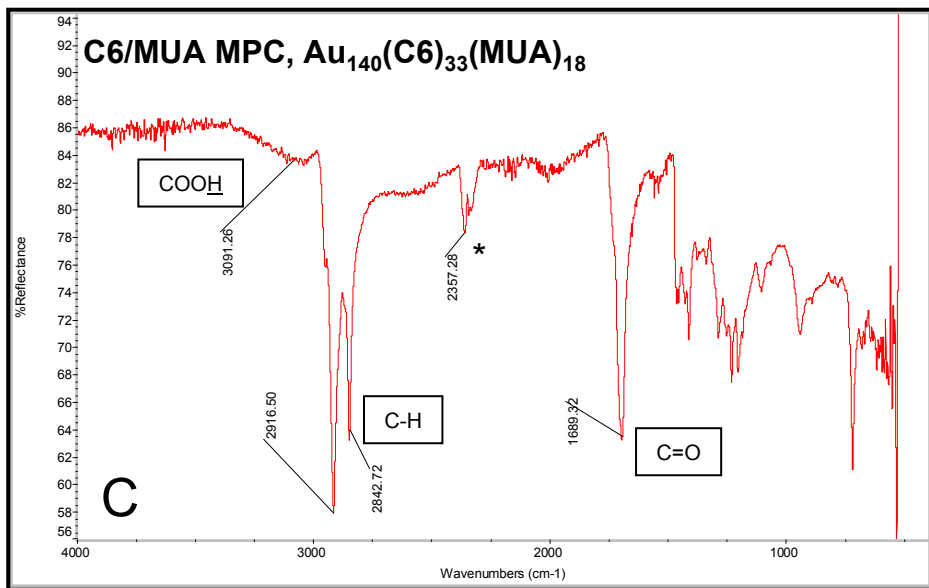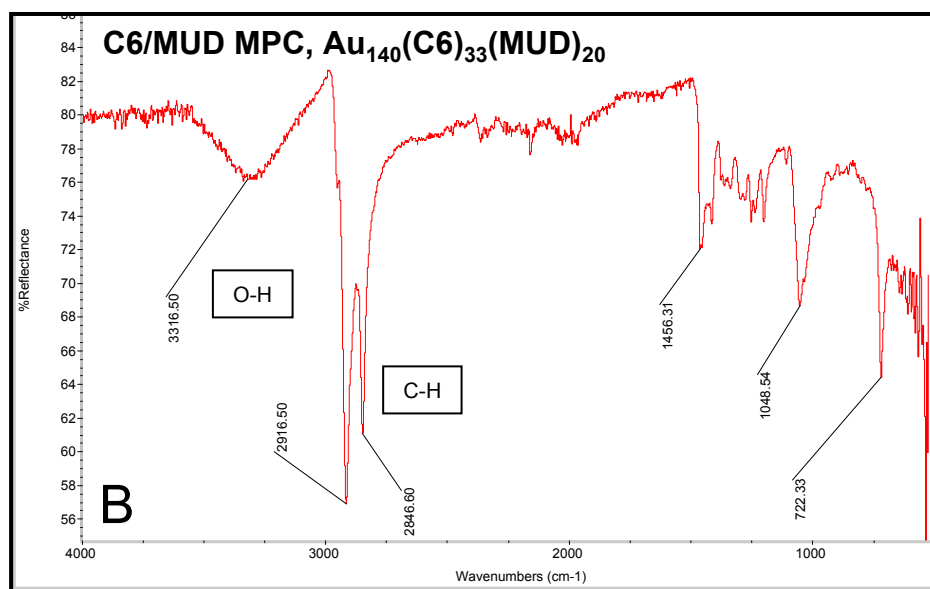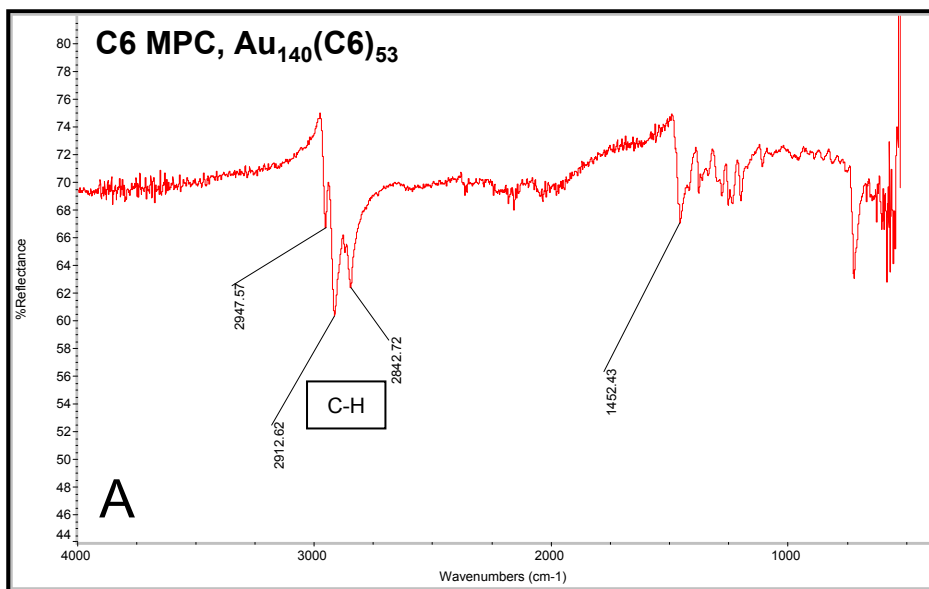
Figure SM-5. IR spectra for (A) C6 MPC starting material, (B) C6/MUD exchanged MPCs, (C) C6/MUA exchanged MPCs, and (D) material after ester coupling. Spectral assignments[†] include the following: υ_{C-H} (2920-2840 cm^{-1}, mp, m); υ_{O-H} (3350-3250 cm^{-1}, sp, vb); υ_{COOH} (3091cm^{-1}, sp, vs, vb); and υ_{RCOOR} (1735 cm^{-1} sp, vs); *residual CO_2 [mp = multiple peaks; sp = single peak; v = very; b= broad; m = medium; s = sharp].

[†]J.B. Lambert, H.F. Shurvell, D. Lightner, R.G. Cooks, "Introduction to Organic Spectroscopy," Macmillan Publishing Company: New York, 1987.