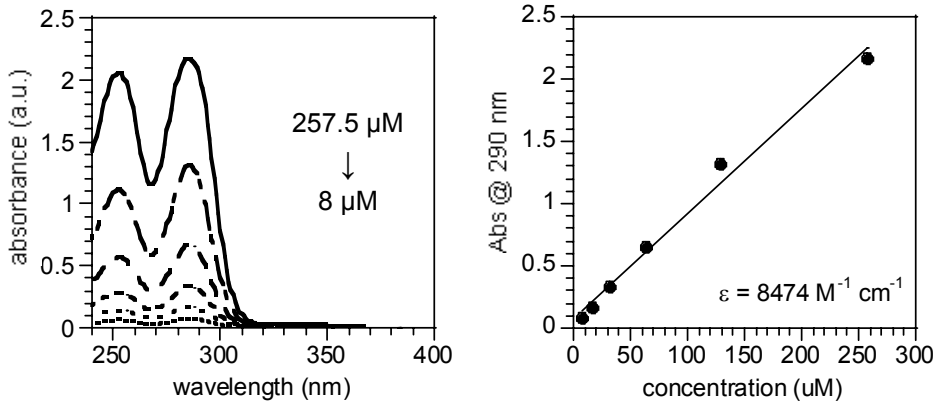
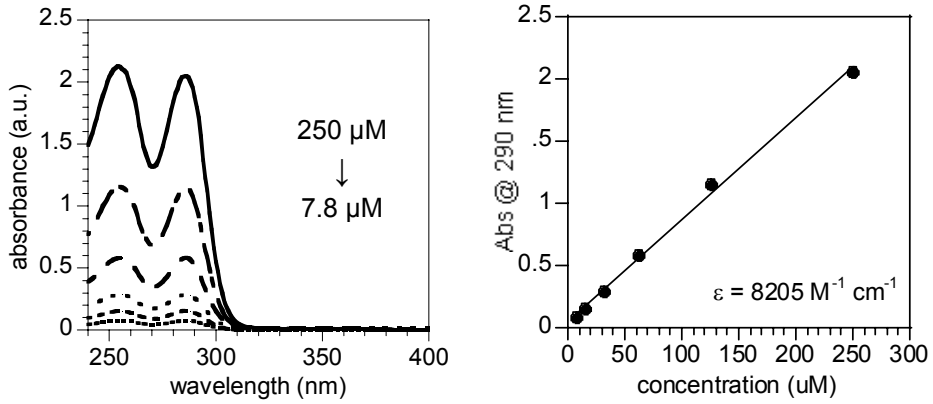
Assembly of Dithiocarbamate-Anchored Monolayers on Gold Surfaces in Aqueous Solutions: Supporting Information

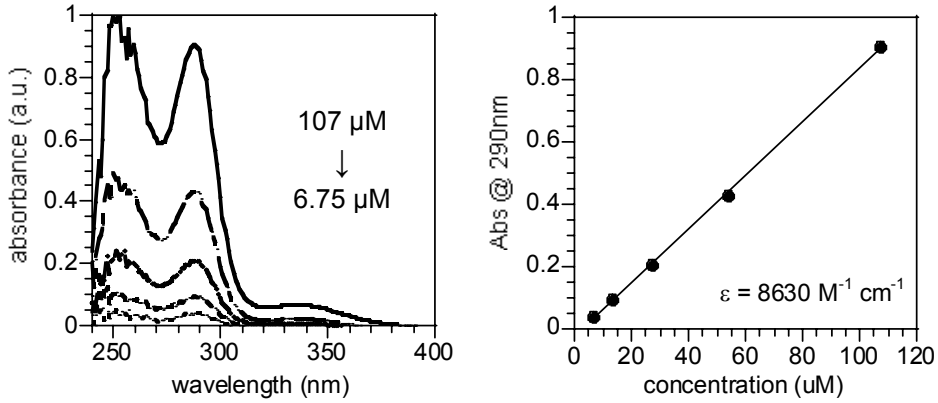
UV absorption spectra of ME-DTC, formed *in situ* in deaerated MeOH (25.7 mM, with 2 equiv. ME) and diluted with deionized water (pH 6) after 30 min.



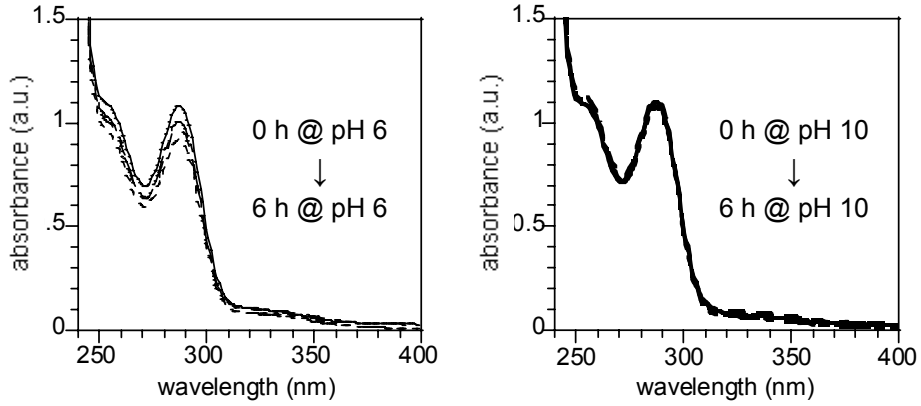
UV absorption spectra of Pro-DTC, formed *in situ* in deaerated MeOH (25 mM, with 2 equiv. Pro) and diluted with deionized water (pH 10) after 30 min.



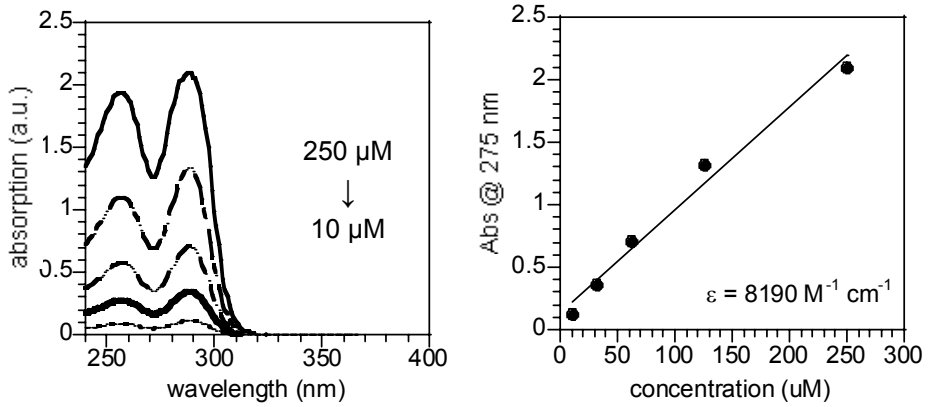
UV absorption spectra of bis-EG6-DTC, formed *in situ* in deaerated DMF (10.7 mM, with 2 equiv. bis-EG6 amine) and diluted with deionized water (pH 10) after 30 min.



Stability of bis-EG6-DTC (125 mM) to air oxidation (pH 6 and pH 10).

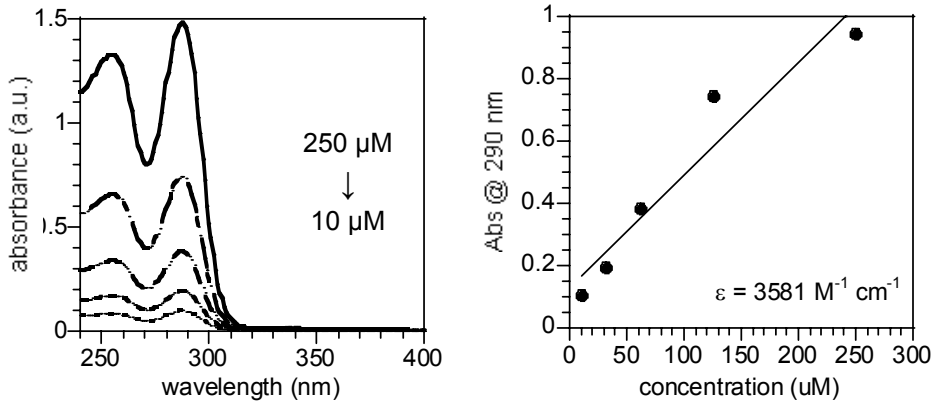


UV absorption spectra of P6R-DTC, formed *in situ* in MeOH (8 mM, with 3 equiv. CS_2 and 1 equiv. Et_3N) and diluted with deionized water (pH 6) to 250 μM after 30 min.



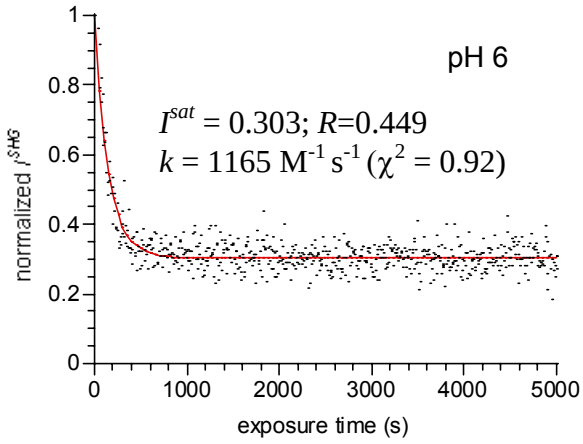
In situ DTC formation was complete after 30 min, by comparison with Pro-DTC.

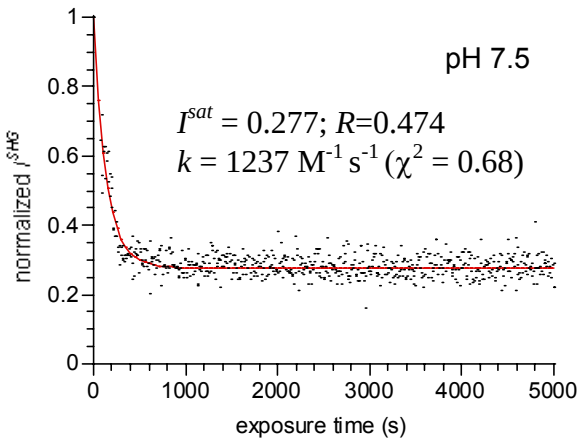
UV absorption spectra of P10LRR-DTC, formed *in situ* in MeOH (4 mM, with 3 equiv. CS_2 and 1 equiv. Et_3N), then diluted with water (pH 6) to 250 μM after 30 min.

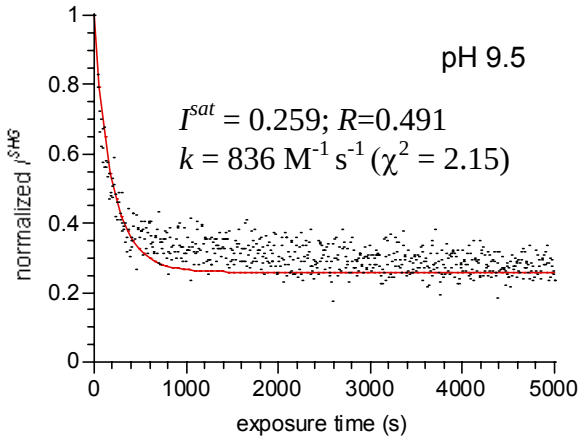


Aqueous solution of P10LRR (250 μM) and CS_2 (3 eq) monitored at RT, prior to serial dilution. Low ε value reveals DTC formation was incomplete after 24 h.

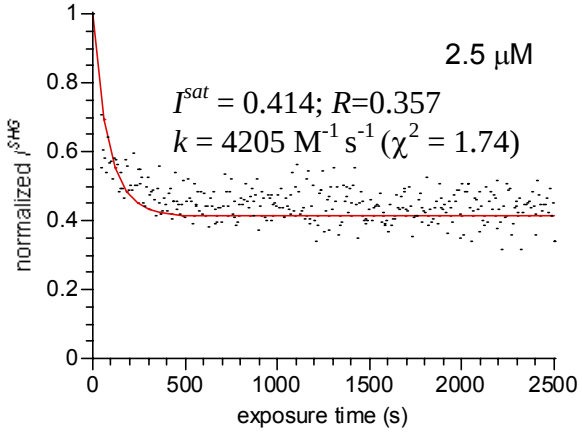
SHG analysis of bis-EG6-DTC adsorption, on freshly cleaned Au surface

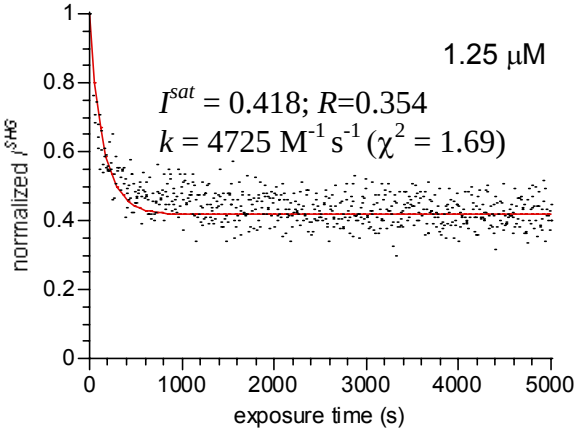




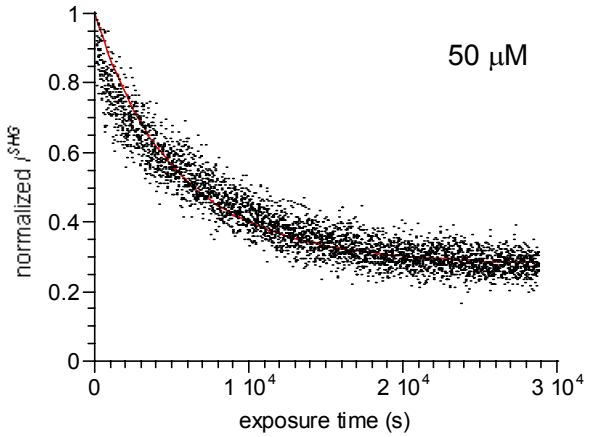


SHG analysis of EG6-SH adsorption



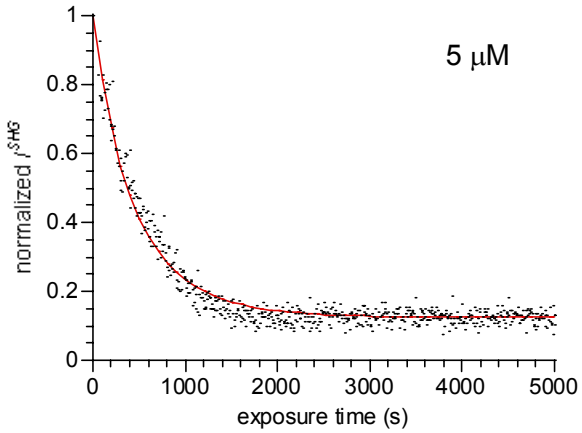


SHG analysis of P10LRR-DTC adsorption (with coadsorption of byproduct)



I^{sat} = 0.277; R=0.474
k = 3 M^{-1} s^{-1} (χ^2 = 8.9)

SHG analysis of ME-DTC adsorption (with coadsorption of byproduct)



I^{sat} = 0.124; R=0.648
k = 319 M^{-1} s^{-1} (χ^2 = 0.78)

Monolayer (ML) estimation of DAMs on Au by XPS. In Ref. 40, Fadley proposed (under the assumption of a non-attenuating adlayer) that the ratio of overlayer-to-substrate signal intensity can be described as

$$\frac{N_l(\theta_{ph})}{N_k(\theta_{ph})} = \frac{\Omega_0(E_l)\times A_0(E_l)\times D_0(E_l)\times \frac{d\sigma_l}{d\Omega}\times d}{\Omega_0(E_k)\times A_0(E_k)\times D_0(E_k)\times \frac{d\sigma_k}{d\Omega}\times \Lambda_e^{subst}(E_k)\cos\theta_{ph}} \times \left(\frac{s_{overl}}{s_{subst}}\right) \qquad \text{(S1)}$$

where $N_l(\theta_{ph})$ and $N_k(\theta_{ph})$ are the peak intensities of the overlayer and substrate (i.e. N 1*s* or S 2*p* and Au 4*f*, respectively), Ω_0 is the acceptance solid angle of the electron analyzer, A_0 the effective area of specimen over which $\Omega_0 \neq 0$, D_0 is the instrument detection efficiency, θ_{ph} is the photoemission angle between surface normal and electron emission direction, $d\sigma_k / d\Omega$ is differential cross-section, which can be calculated using tabulated Scofield cross-sections and the Reilman asymmetric parameter, $\Lambda_e^{subst}(E_k)$ is the inelastic mean free pass (IMFP) of the substrate photoelectron in the substrate, s_{overl} is the mean surface density of atoms in which peak *l* originates in cm^{-2}, s_{subst} is the mean surface density of substrate atoms in cm^{-2}, s_{overl}/s_{subst} is the fractional monolayer coverage of the atomic species in which peak *l* originates, and *d* is the mean separation between layers of density *s* in the substrate.

The short HE chains allow the Au 4*f* signal intensities to be measured with minimal extinction, and permit a straight application of the non-attenuating adlayer approximation to determine adlayer coverage in terms of ML, i.e. the ratio of adatoms to surface Au atoms. For simplicity, the surface was assumed to be equivalent to a Au(111) plane. Eq. S1 can then be modified so that the adlayer coverage (based on the S 2*p* peak) can be defined as:

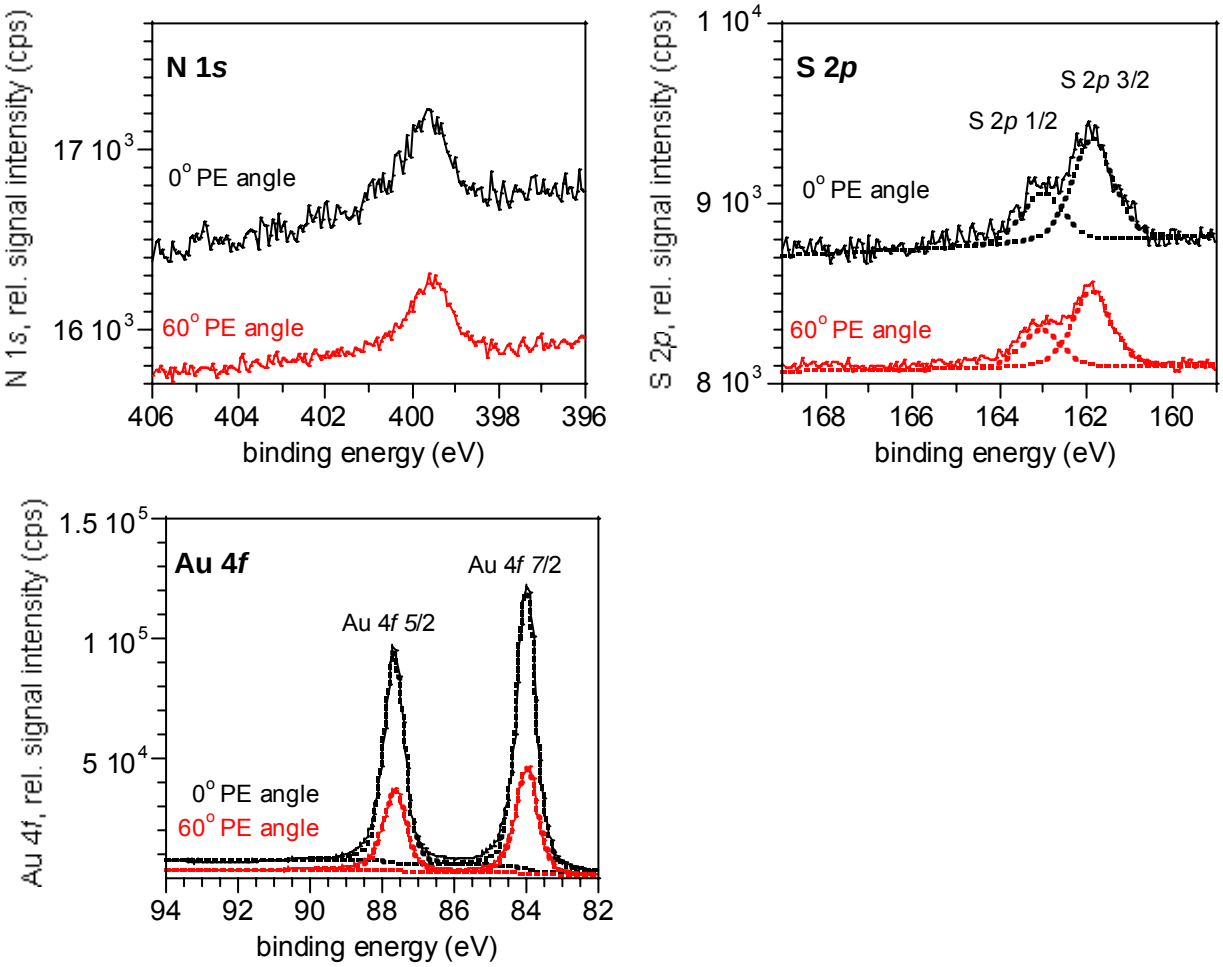
$$\theta = \frac{N_{S_{2p}}}{N_{Au_{4f}}} \frac{\frac{d\sigma_{Au_{4f}}}{d\Omega}\times \Lambda_e^{Au}(KE_{Au_{4f}})\cos\theta_{ph}}{\frac{d\sigma_{S_{2p}}}{d\Omega}\times d} \qquad \text{(S2)}$$

where $N_{S_{2p}}$ and $N_{Au_{4f}}$ are the intensities of the S 2*p* and Au 4*f* peaks respectively, $\Lambda_e^{Au}(KE_{Au_{4f}})$ is the IMFP of the Au 4*f* photoelectron in bulk Au (15.78 Å), and *d* is the lattice spacing between Au(111) planes (1.29 Å). The N 1*s* peak intensity can be used to calculate ML coverage in a similar fashion.

XPS spectra of DAMs on Au

All spectra were acquired using monochromatic Al Kα radiation (1486.58 eV) at photoemission (PE) angles of 0° and 60°, with an acquisition time of 4.8 s for N and S, or 0.4 s for Au.

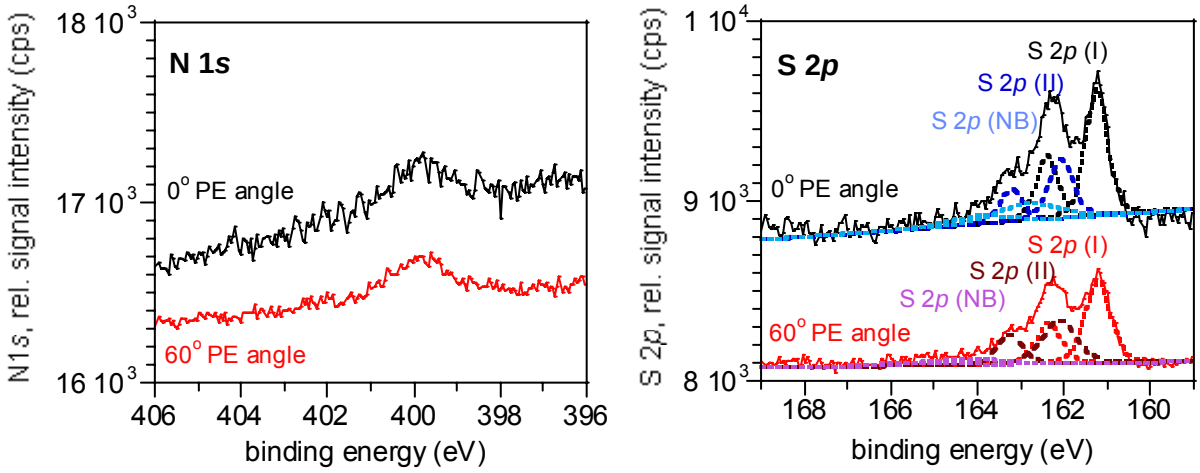
Bis-HE-DTC on Au:



	area (%)	N 1*s*	S 2*p*	Au 4*f*	S/N*	S/Au	ML	N	S
0°		1.42	2.97	38.74	2.09	0.077		0.44	0.46
60°		2.32	4.37	28.64	1.88	0.153		0.48	0.43

*theor. value = 2.0

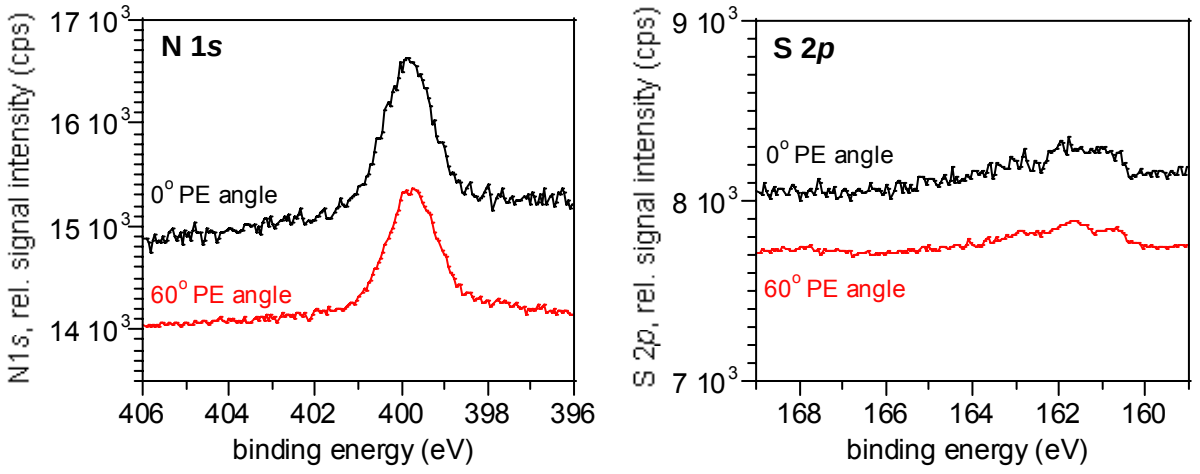
ME-DTC on Au:



	area (%)	N 1*s*	S 2*p*	Au 4*f*	S/N*	S/Au	ML	N	S
0°		1.20	4.35	55.00	3.62	0.079		0.26	0.52
60°		1.61	5.26	34.66	3.26	0.152		0.28	0.45

*theor. value = 2.0

P10LRR-DTC on Au:



	area (%)	N 1*s*	S 2*p*	Au 4*f*	S/N*	S/Au	ML	N	S
0°		7.3	1.3	40.8	0.18	0.032		0.07	0.19
60°		8.6	2.0	25.0	0.23	0.080		0.07	0.24

*theor. value = 0.13