

## Supporting Information

**Table 1S.** Main experimental wavenumbers ( $\text{cm}^{-1}$ ) and assignments of the bands observed in the Raman spectrum of neat liquid sample and the SERS spectra of DT8 adsorbed on Ag and Au NPs. The assignments of the main bands are also presented.

Wavenumbers ( $\text{cm}^{-1}$ ) of Raman spectra			Assignments <sup>a</sup>
Neat Liquid Sample	SERS on Ag ( $10^{-6}$ M)	SERS on Au ( $8 \times 10^{-6}$ M)	
2925m	2920m	2902m	$\nu_{\text{as}}(\text{CH})/\text{FR}$
2898sh	2889sh		$\nu_{\text{as}}(\text{CH})$
2850m	2856m	2845m	$\nu_{\text{s}}(\text{CH})$
2570s		2570w	$\nu(\text{SH})$
1437s	1437m	1436s	$\delta(\text{CH}_2)$
	1416sh		$\delta(\text{CH}_2)$
1300m	1297m	1297s	$\omega(\text{CH}_2)$
1247vw	1237w		$\tau(\text{CH}_2)$
	1200sh	1181w	$\tau(\text{CH}_2)$
	1078m	1081s	$\nu_{\text{T}}(\text{CC})$
1081m			$\nu_{\text{G}}(\text{CC})$
1022w	1009m	1008w	$\nu_{\text{T}}(\text{CC})$
	929w	906sh	$\rho(\text{CH}_2)$
	897w	875w	$\rho(\text{CH}_2)$
858m	868w		$\rho(\text{CH}_2)$
738m			$\nu_{\text{T}}(\text{CS})$
	688vs	703w	$\nu_{\text{T}}(\text{CS})$
705sh			$\nu_{\text{T}}(\text{CS})$
653s		640m	$\nu_{\text{G}}(\text{CS})$
	618s		$\nu_{\text{G}}(\text{CS})$
		280vs	$\nu(\text{Au-S})$
	220vs		$\nu(\text{Ag-S})$
		170w	$\nu(\text{Au-S})$

<sup>a</sup> $\nu$ : stretching,  $\delta$ : bending,  $\omega$ : wagging,  $\tau$ : twisting,  $\rho$ : rocking

(vs): very strong, (s): strong, (m): medium, (w): weak, sh: shoulder

## Calculation of tilt angles for all the investigated dithiols from the spectral data

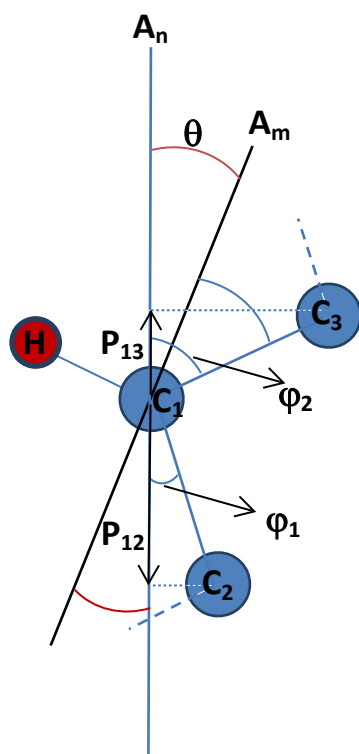


Figure 1S

Figure S1 displays a fragment of an aliphatic linear chain undergoing a certain inclination of its main axis ( $A_m$ ) with respect to the normal axis ( $A_n$ ) to the metal surface. The inclination is given by the tilt angle  $\theta$  (Figure 1S). The overall intensity of  $\nu(\text{CC})$  and  $\nu(\text{CH})$  modes will be modified on the basis of the different projections of the corresponding normal modes in  $A_n$ . Taking into account the chain fragment represented in Figure 1S, we can see that the deviation of the molecule from the normal leads to the distinction of two different CC bonds,  $\text{C}_1\text{C}_2$  and  $\text{C}_2\text{C}_3$ , with two different projections ( $P_{13}$  and  $P_{12}$ ) given by two different angles  $\varphi_1$  and  $\varphi_2$  which lead to the following expressions:

$$P_{13} = C_1^- C_3 \cos \varphi_2 \quad \text{and} \quad P_{12} = C_1^- C_2 \cos \varphi_1$$

where  $\varphi_1$  and  $\varphi_2$  can be related to the tilt angle  $\theta$  in the following way, assuming that the angle between  $C_1^- C_3$  and  $C_1^- C_2$  is of  $109.5^\circ$  as corresponds to a  $\text{sp}^3$  hybridization of C atom in the polymethylene chain:

$$\varphi_1 = 35.25^\circ - \theta \quad \text{and} \quad \varphi_2 = \theta + 35.25^\circ$$

then:

$$P_{C_1C_2} = C_1^- C_2^- \cos (35.25^\circ - \theta)$$

$$P_{C_1C_3} = C_1^- C_3^- \cos (\theta + 35.25^\circ)$$

In the case of the CH stretching vibration we have the following projection for all the CH bonds (Figure 1S):

$$P_{CH} = C_1^- H^- \cos (90^\circ - \theta)$$

The enhancement intensity associated to  $\nu(\text{CC})$  and  $\nu(\text{CH})$  modes of dithiols adsorbed onto a metallic surface, with respect to the free molecule in liquid state, is related to the projections on the normal axis  $A_n$ , by considering the selection rules (see reference 33 of main text) that predict a higher enhancement for those vibrational modes bearing a strong polarizability projection in the normal direction, since the electromagnetic near field is highly polarized in the direction perpendicular to the surface. Then we can obtain the following expressions in function of the tilt angle:

$$I_{CC} = I_{C_1C_2}^0 \cos (35.25^\circ - \theta) + I_{C_1C_3}^0 \cos (\theta + 35.25^\circ)$$

$$I_{CH} = I_{CH}^0 \cos (90^\circ - \theta)$$

Where  $I_{C_1C_2}^0$  and  $I_{C_1C_3}^0$  correspond to the Raman intensity contribution of  $\nu(\text{CC})$  modes of  $\text{C}_1\text{-C}_2$  and  $\text{C}_2\text{-C}_3$  bonds in the molecule out of the metal influence, i.e in liquid state. Since both bonds are equivalent in liquid state, then  $I_{C_1C_2}^0 = I_{C_2C_3}^0 = I_{CC}^0$ , and  $I_{CC}$  can be expressed as follows:

$$I_{CC} = I_{CC}^0 \cos (35.25^\circ - \theta) + I_{CC}^0 \cos (\theta + 35.25^\circ)$$

and for a polymethylene chain containing  $n$  C atoms:

$$I_{CC} = \frac{n}{2} I_{CC}^0 \cos (35.25^\circ - \theta) + \frac{n}{2} I_{CC}^0 \cos (\theta + 35.25^\circ)$$

$$I_{CH} = n I_{CH}^0 \cos (90^\circ - \theta)$$

From the above expressions we can get the following expression:

$$\frac{I_{CC}}{I_{CH}} = \left[ \frac{0.82(n-1)\cos \theta - 0.58\sin \theta}{-n\sin \theta} \right] \frac{I_{CC}^0}{I_{CH}^0}$$

and then:

$$\frac{\frac{I_{CC}}{I_{CH}^0}}{\frac{I_{CC}^0}{I_{CH}^0}} = \frac{I_{CC}I_{CH}^0}{I_{CC}^0I_{CH}^0} = R = \left[ \frac{0.82(n-1)\cos\theta - 0.58\sin\theta}{-n\sin\theta} \right]$$

Finally, the tilt angle  $\theta$  can be calculated from the  $R$  ratio and  $n$  by the following expression:

$$\tan\theta = \frac{0.82(n-1)}{0.58-nR} \quad (1S)$$

The values of  $R$  measured from the spectra shown in Figures 3-5 obtained by exciting at 785 nm and those obtained at 532 nm lead to the  $R$  and tilt angle values for all the studied dithiols shown in Table 2S.

**Table 2S**

$R$  values calculated from the SERS spectra of dithiols at concentration  $10^{-4}$  M (785 nm) and  $5 \times 10^{-5}$  M (532 nm) and tilt angles ( $\theta$ ) calculated from Equation 1S.

Dithiol	532 nm		785 nm	
	R	$\theta$	R	$\theta$
DT6	3.16±0.15	8.7°	4.61±0.18	10.4°
DT8	10.47±0.48	5,3°	12.26±0.61	3.8°
DT10	13.04±0.65	5.4°	10.20±0.51	4.6°