

## Supporting Information

**Table 1S.** FT-IR data ( $\bar{\nu}/\text{cm}^{-1}$ ) of HPW, Cys and (Cys)PW

Compound	$\bar{\nu}(\text{COO}^-)$	$\bar{\nu}(\text{CH}_2)$	$\bar{\nu}(\text{C-O})$	$\bar{\nu}(\text{C-N})$	$\bar{\nu}(\text{P-O}_a)$	$\bar{\nu}(\text{W-O}_d)$	$\bar{\nu}(\text{W-O}_b\text{-W})$	$\bar{\nu}(\text{W-O}_c\text{-W})$
HPW	-	-	-	-	1079	972	887	753
Cys	1740, 1512	1432, 1400	1218	1138	-	-	-	-
(Cys)PW	1731, 1510	1470	1251	1137	1073	967	883	750

O<sub>a</sub> Central oxygen  
 O<sub>b</sub>, O<sub>c</sub> Bridging oxygen  
 O<sub>d</sub> Terminal oxygen

**Table 2S.** Electrochemical parameters extracted from CVs (Fig. 2B) on bare poly Au and poly Au SAM- modified electrodes in the presence of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  (0.5 mM) in PBS (0.11 M, pH 3).

Electrode	$i_{p,a}$ ( $\mu\text{A}$ )	$\Delta E_p$ (mV)
Bare poly Au	6.42±0.11	63±5
poly Au- Cys SAM	5.79±0.06	88±10
poly Au- HPW SAM	2.31±0.18	127±8
poly Au- (Cys)PW SAM	8.24±0.24	61±4