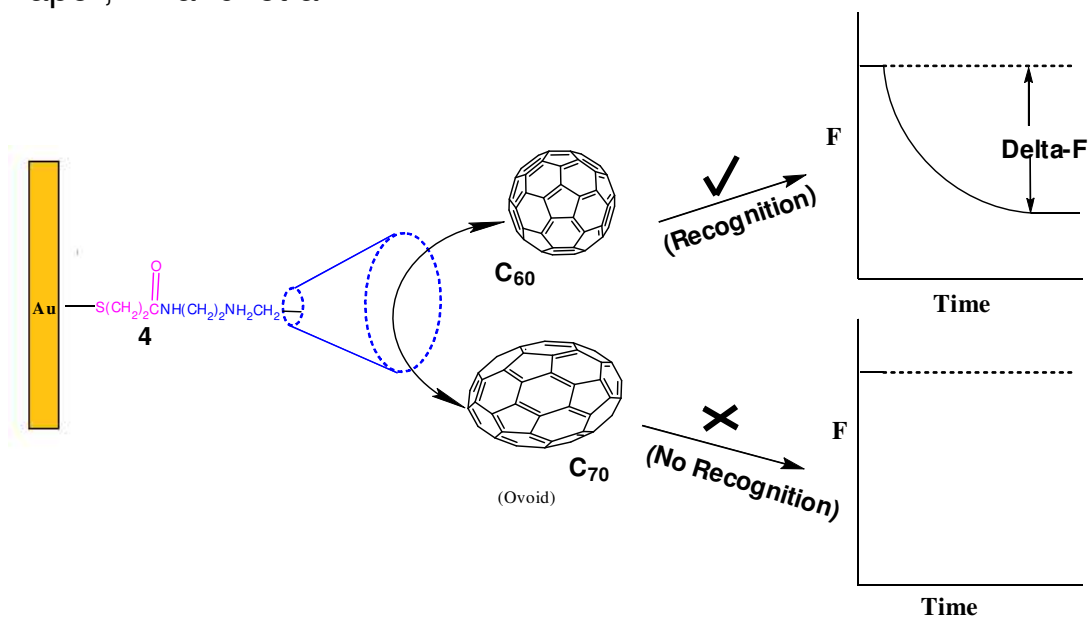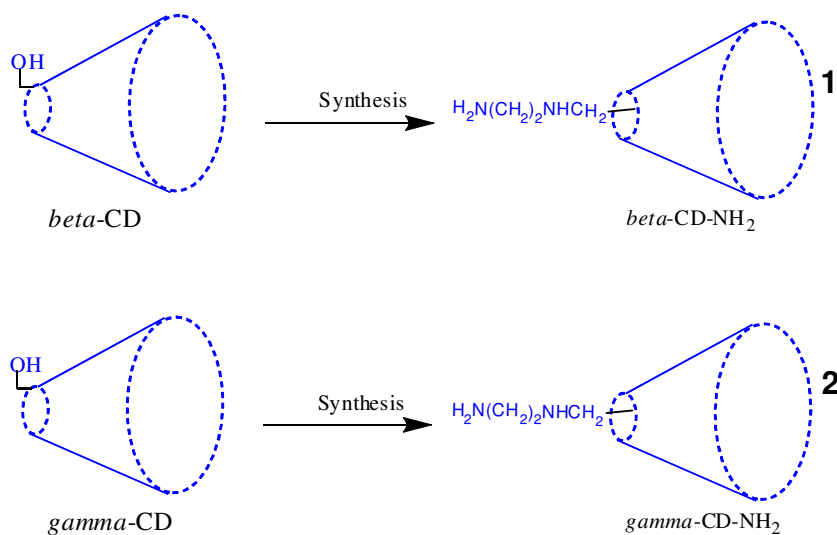# Supporting Information

Size-exclusive Nanosensor for Quantitative Analysis of Fullerene C_{60}: A Concept Paper, Kikandi et al


Scheme 1: *beta* -CD assembly on QCM (Au), C_{60} recognition chemistries and particle count measurement from changes in frequency (Delta-F, Hz) versus time(s)


Supplementary Figure 1A: Synthesis of *beta-CD* -NH$_2$, **1** and *gamma-CD* -NH$_2$ **2.** Details on the synthesis protocol can in found in reference(1)
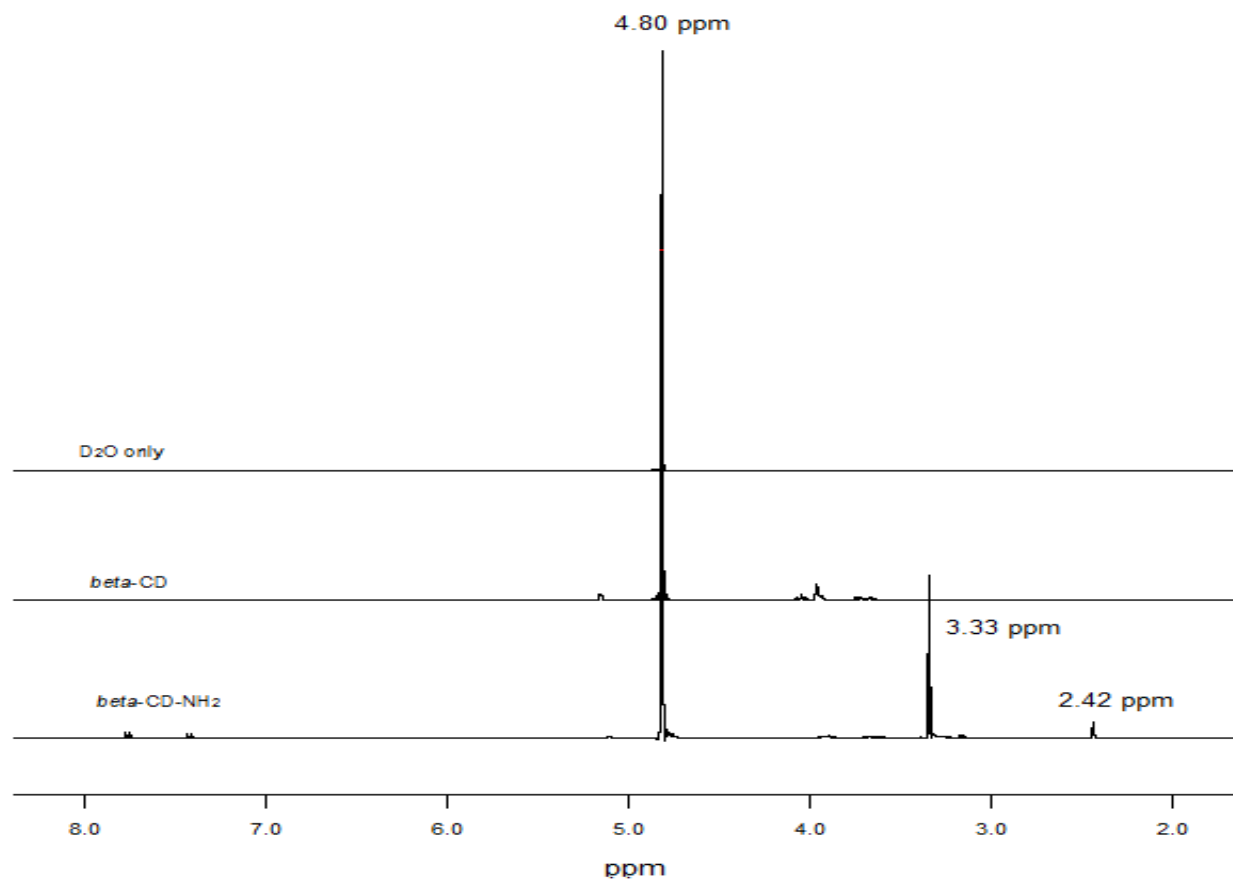
Supplementary Figure 1B: ^{1}H-NMR Spectra of *beta*-CD-NH$_2$ **1** in D$_2$O at 25 °C. D$_2$O and *beta*-CD spectra are overlaid for comparison purposes. ^{1}H-NMR Spectra of the *gamma*-CD-NH$_2$ **2** showed similar spectra (spectra not included here)
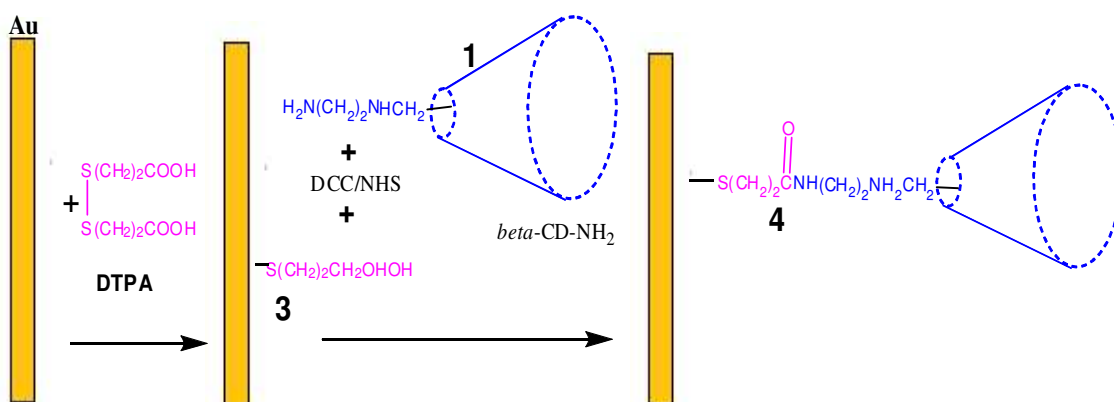
Supplementary Figure 1C: Beta-cyclodextrin assembly on QCM (Au**). In step 1 QCM (Au) is reacted with 3, 3' dithiopropionic acid (DTPA) to yield component **3** consisting of Au-S bond on one end and a carboxyl group on the other end. Carboxyl group is reacted with *beta*-CD-NH$_2$ via DCC/NHS chemistry to yield (Au)-S–(CH$_2$)$_2$-CONH-*beta*–CD sensor **4**.
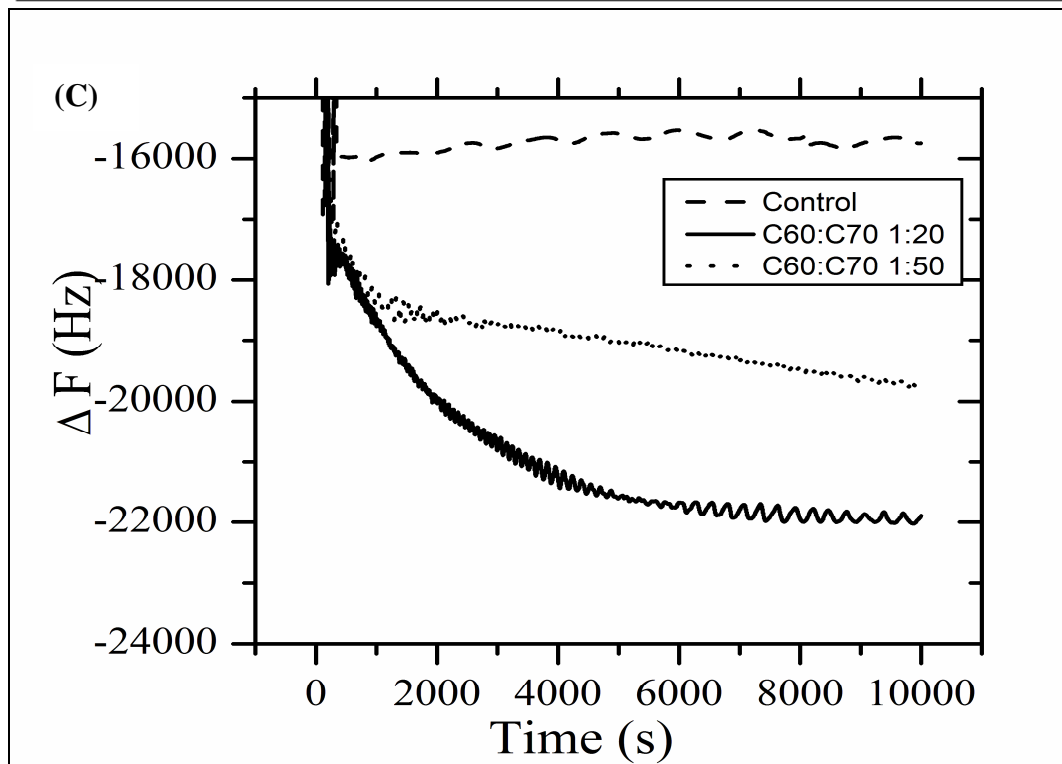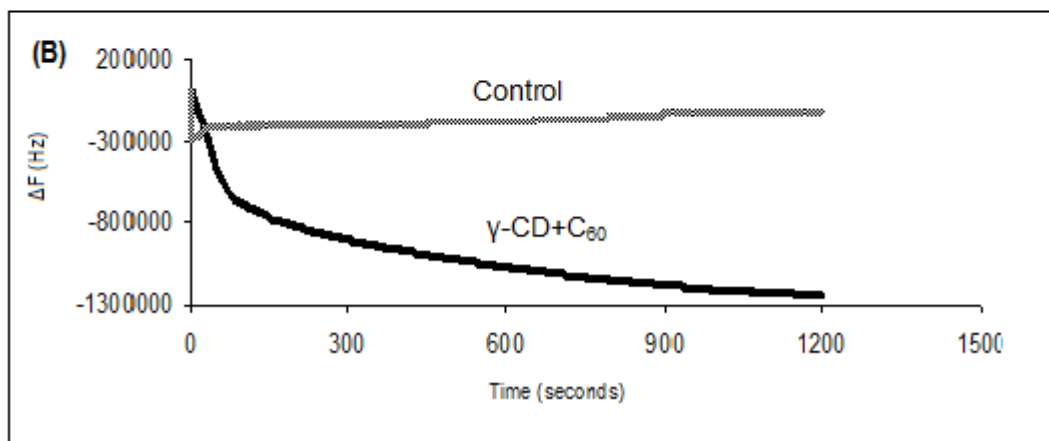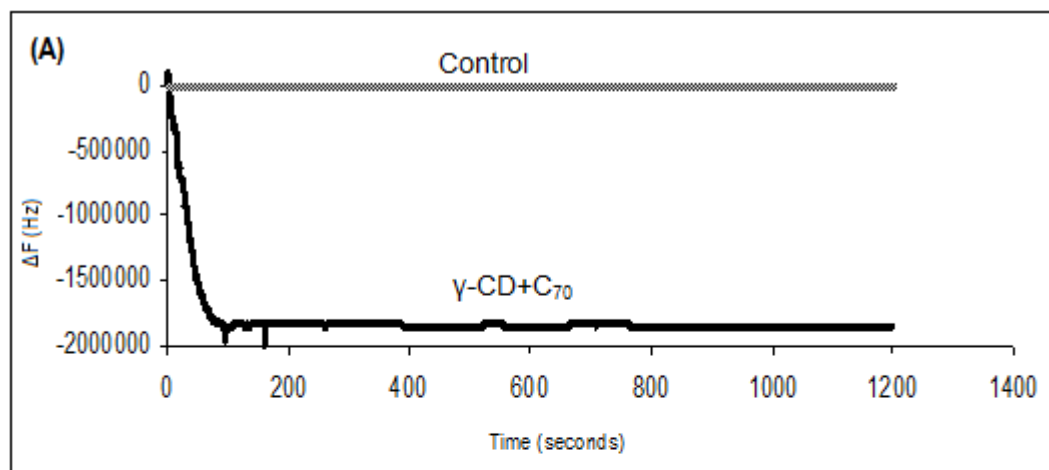
Supplementary Figure 2: Frequency *vs* time for QCM (Au)-S–$(CH_2)_2$-CONH-beta–CD sensor, **4** in presence of fullerene 0.14 mg/ml C_{60} or C_{70}, [0.07mg/ml]C_{60}/C_{70} mixture and control (toluene). According to Saurbrey Equation, ΔF is inversely proportional to Δm, C_{70} having a

larger mass (840.749 g/mol) shows a larger ΔF (closely packed system (111), ΔF 1 Hz = 1.34 ng, Area = 0.2 cm^2, Avogadro's # $6.022e^{23}$, molar mass of C_{60} = 720.64 g/mol).

Sensor Surface Characterization: The chemistry and morphology of the supramolecular assembly onto QCM was confirmed using two techniques: Field Emission Scanning Electron Microscope (FESEM) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The FESEM used was a Zeiss Supra™ 55VP, which provides ultra high resolution imaging(1.7 nm - 4 nm) over the complete voltage range(2). Single fullerenes may not be detected by this FESEM since they are less than 1nm. However, any cumulative aggregation into clusters greater than the detection limit could be observable and hence its suitability for our sensor characterization. ToF-SIMS on the other hand has previously been used to characterize the chemistry of thiol based self assembled monolayers (SAMs)(3-7). ToF-SIMS has high chemical specificity allowing for the detection of molecular species at surfaces along with the interaction of the SAM with the metal substrate. The sampling depth of SIMS for surface analysis is typically between 1 and 5 nm. Using ToF analysis allows for a high mass resolution (ca. M/ΔM = 7000 at m/z = 27) over a large mass range (e.g. 1-10,000 Da). ToF-SIMS experiments were performed on an ION TOF V 5-100 ION TOF gmbh equipped with Bi, Cs, and C_{60} primary ion beam sources. Using this system, a Bi_3^{++} primary ion beam was utilized as the analysis gun for both static and imaging analysis in this study and was operated in the high current bunched mode at 25kV. Analysis area variation occurred during sample analysis therefore the primary ion dose varied per raster area. The target current was measured by a Faraday cup to be 0.25 pA. Each raster area was divided into 128 x128 pixels and analyzed in the negative ion mode with a cycle time of 120 μs. The mass analyzer was operated in the high mass resolution mode (Analyzer Extractor 2000V, Analyzer Energy 1000V) and the secondary ions were detected by a microchannel plate detector with a post-acceleration energy of 10 kV.

Supplementary Table 1: Fragment ions used for the identification of the DPTA functionalized gold QCM

| Fragment	m/z	Origin
$C_2H_4S^-$	60	Dithiodipropionic Acid
$C_3H_5SO_2^-$	105	Dithiodipropionic Acid
Au^-	197	Gold Substrate
$C_6H_9S_2O_4^-$	209	Dithiodipropionic Acid
$C_{12}H_{19}S_4O_8^-$	419	Dithiodipropionic Acid
Au_3^-	591	Gold Substrate

:
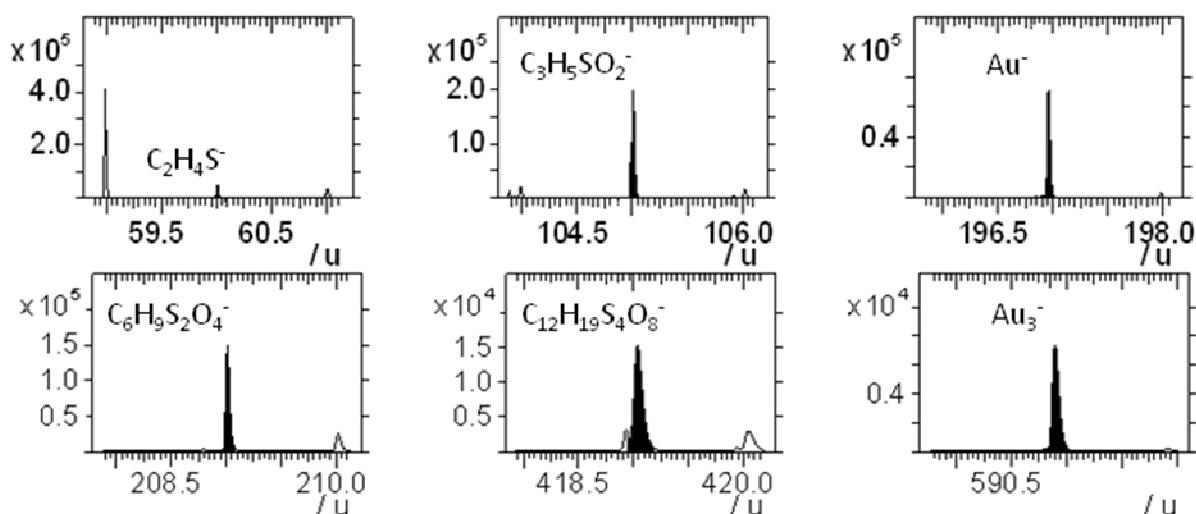
Supplementary Figure 3: ToF-SIMS of representative 3, 3' dithiopropionic acid (DTPA) peaks ($C_2H_4S^-$ m/z 60; $C_3H_5SO_2^-$ m/z 105; $C_6H_9S_2O_4^-$ m/z 209 & $C_{12}H_{19}S_4O_8^-$ m/z 419) and the gold substrate fragmentation ions (Au$^-$ m/z 197 & Au$_3^-$ m/z 591) acquired in the negative ion acquisition mode

Supplementary Table 2: Fragment ions used for identification in the (Au)-S-$(CH_2)_2$-CONH-β-CD sensor before and after exposure to fullerene solution. *Molecular formula for fragment ion obtained from Rubara, *et al.* (8)

| Fragment	m/z	Origin
*$C_8H_7O^-$	119	Cyclodextrin
Au$^-$	197	Gold
*$C_8H_{13}O_7^-$	221	Cyclodextrin
*$C_{14}H_{23}O_{12}^-$	383	Cyclodextrin
Au$_3^-$	591	Gold
C_{60}^-	720	Fullerene
*$C_{26}H_{43}O_{22}^-$	707	Cyclodextrin
*$C_{42}H_{72}O_{35}^-$	1137	Cyclodextrin
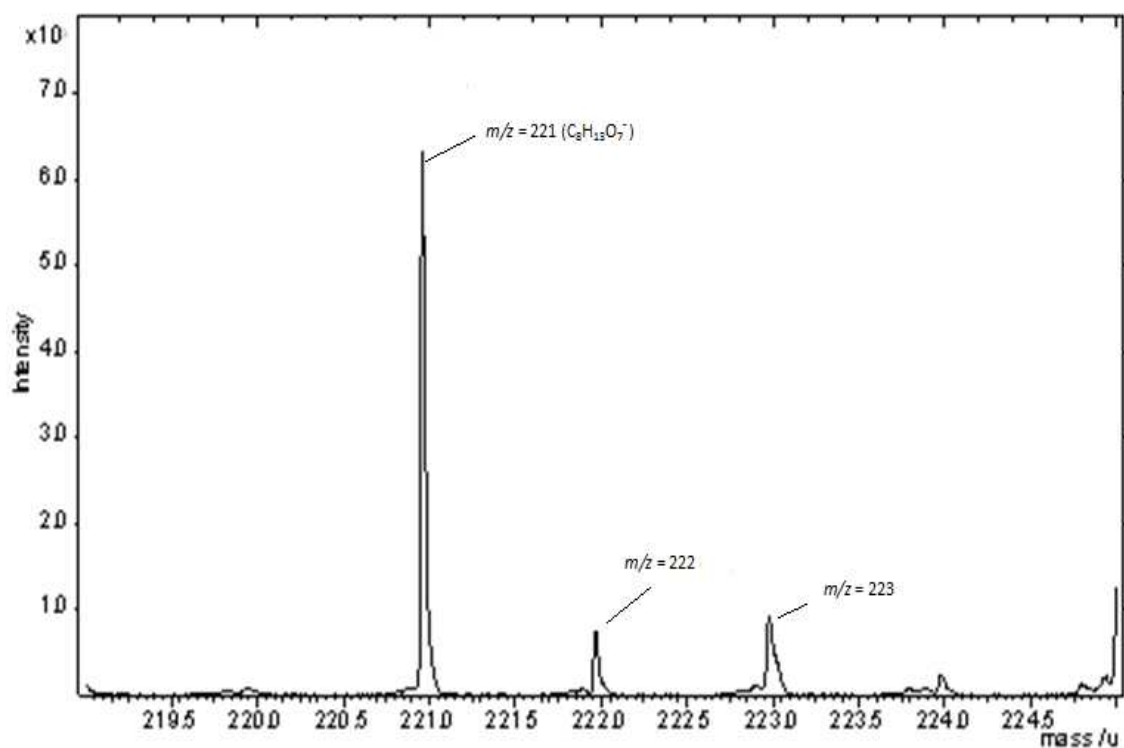
Supplementary Figure 4: ToF-SIMS of $C_8H_{13}O_7^-$ representative cyclodextrin peak and other fragmentation ions acquired in the negative ion acquisition mode
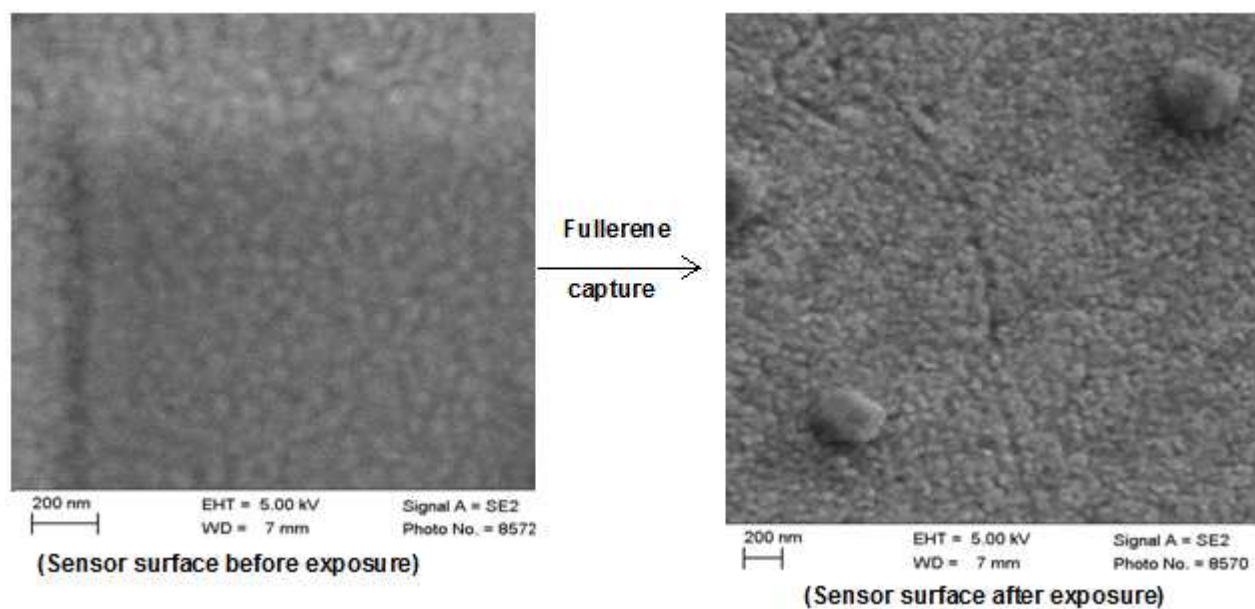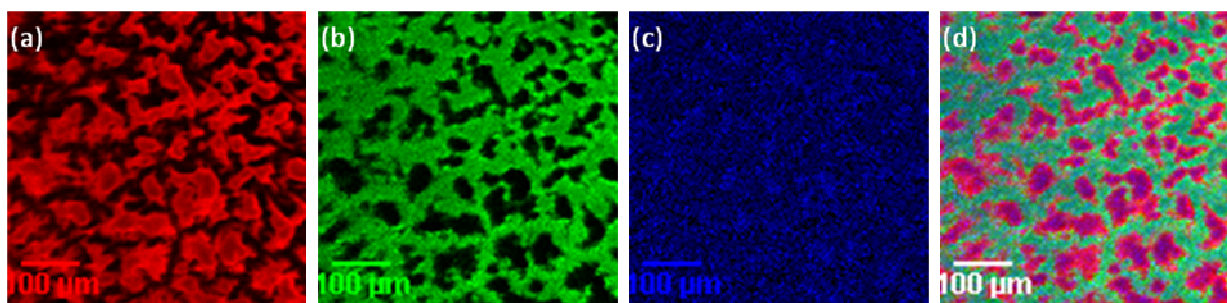

Supplementary Figure 5: SEM images of the mass-sensitive sensor **4** surface before and after exposure to fullerene C_{60} nanomaterials. FESEM (2) was used to confirm the presence of fullerene

clusters on the QCM sensor before and after exposure to C_{60}. Results showed near spherical clusters $\geq$ 200 nm as approximated from the SEM images (**Supplementary Figure 5**) suggesting a few hundreds of C_{60} particles per cluster. This was a confirmation of β-CD captured C_{60} particle clusters. It is likely that the fullerene clusters were captured partially or that aggregation occurred on single captured fullerenes. Aggregation is known to be a slow process beyond this experiment's control but the near spherical nanoparticle images is consistent with C_{60} clustering behavior[1].
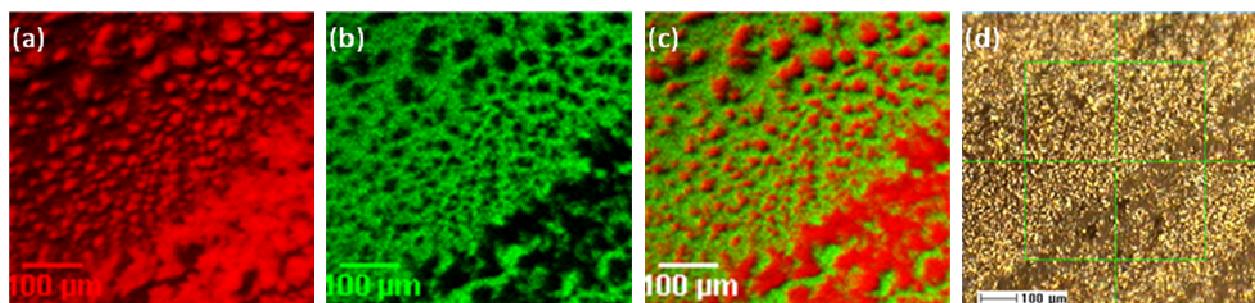
Supplementary Figure 6A: False color ToF-SIMS chemical images of QCM (Au)-S-$(CH_2)_2$-CO_2H (a) Dithiodipropanoic Acid; (b) Gold (Au) (c) Overlay of two colored images; (d) Optical image of analyzed area taken in the analysis chamber. Colored overlay image prepared using Ion Image® Software Package, scale bar added using ImageJ(9).

Supplementary Figure 6B: False color ToF-SIMS chemical image of QCM (Au)-S-$(CH_2)_2$-CONH-*β-CD β-CD* (a) Dithiodipropanoic Acid; (b) Gold (Au); (c) Cyclodextrin (d) Overlay of three colored images. Colored overlay image prepared using Ion Image® Software Package, scale bar added using ImageJ(9).
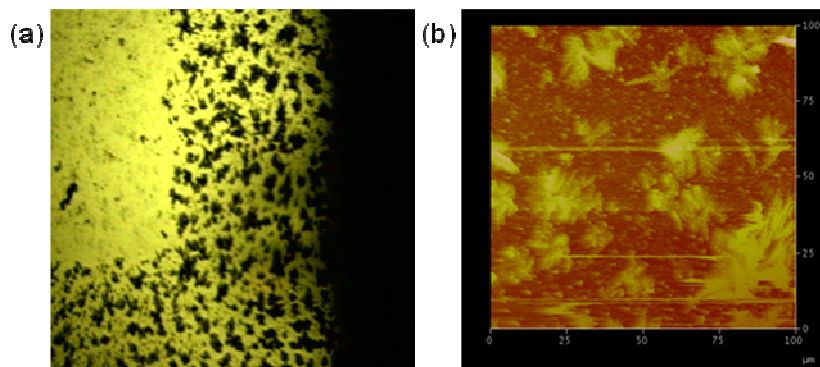
Supplementary Figure 7. (a) Camera image of area analyzed during ToF-SIMS analysis of QCM (Au)-S-$(CH_2)_2$-CONH-*β-CD β-CD.* Note the area which has no black islands indicates the area analyzed by ToF-SIMS; (b) AFM image of an area from camera image which contained the black islands.

Cited references

(1)   Liu, Y.; Yang, Y. W.; Chen, Y., Thio[2-(benzoylamino)ethylamino-beta-CD fragment modified gold nanoparticles as recycling extractors for [60]fullerene. *Chemical Communications* 2005, (33), 4208-4210.
(2)   http://www.zeiss.com/c1256e4600305472/Contents-Frame/c4bc1c66687fdce1c1256fe100420194.
(3)   Hagenhoff, B.; Benninghoven, A.; Spinke, J.; Liley, J.; Knoll, W., Time-of-Flight Secondary Ion Mass Spectrometry Investigations of Self-Assembled Monolayers of Organic Thiols, Sulfides, and Disulfides on Gold Surfaces. *Langmuir* 1993, *9*, 1622-1624.
(4)   Sun, L.; Gardella, J. A., Oxidation-Assisted Secondary Ion Mass Spectrometry Methodology to Quantify Mixed Alkylthiol Self-Assembled Monolayers on Gold: Applications to Competitive Chemical Adsorption. *Langmuir* 2002, *18*, (24), 9289-9295.
(5)   Wolf, K. V.; Cole, D. A.; Bernasek, S. L., High- Resolution TOF-SIMS Study of Varying Chain Length Self-Assembled Monolayer Surfaces. *Analytical Chemistry* 2002, *74*, 5009-5016.
(6)   Zhu, Z.; Allara, D. L.; Winograd, N., Chemistry of metal atoms reacting with alkanethiol self-assembled monolayers. *Applied Surface Science* 2006, *252*, 6686-6688.
(7)   Hagenhoff, B.; Benninghoven, A.; Spinke, J.; Liley, M.; Knoll, W., Time-of-flight secondary ion mass spectrometry investigations of self-assembled monolayers of organic thiols, sulfides, and disulfides on gold surfaces. *Langmuir* 1993, *9*, (7), 1622-1624.
(8)   Rabara, L.; Aranyosiova, M.; Velic, D., Supramolecular host-guest complexes based on cyclodextrin-diphenylhexatriene. *Applied Surface Science* 2006, *525*, 7000-7002.
(9)   Collins, T. J., ImageJ for microscopy. *BioTechniques* 2007, *43*, S25-S30.