Supporting Information

The adsorption of 4-n-nonylphenol, carvacrol and ethanol onto iron oxide from non-aqueous hydrocarbon solvents

Richard M. Alloway, Jennings Mong, Izaak W. Jephson, Mary H. Wood, Michael T. L. Casford, Peter Grice, Sorin V. Filip, Ibrahim E. Salama, Colm Durkan and Stuart M. Clarke

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Comparison between UV/vis and qNMR as analytical techniques for adsorption isotherms

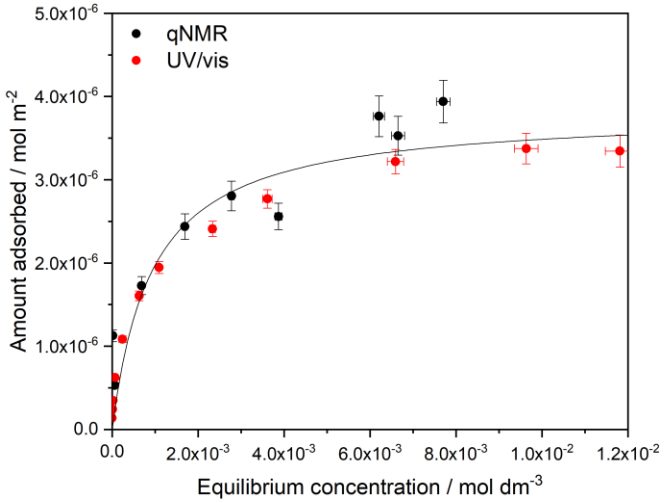

Figure S1. Comparison between UV/vis (black) and qNMR (red) as an analytical technique for measuring the adsorption isotherm of 4NP onto iron oxide from dodecane. Data are shown as points and a Langmuir fit is shown as a line. The $\overline{\text{NRMSD}}$ value is 0.07.

Characterization of iron oxide substrates

Powder

X-Ray Diffraction (XRD) was performed on the iron (III) oxide powder used for the adsorption isotherm experiments. The data, shown in Figure S2, index well onto the crystal structure of hematite (Fe_2O_3). The literature also report hematite for this product, with a small amount of magnetite (Fe_3O_4) at 7.5%[1].

Elemental analysis, using Atomic Emission Spectroscopy (AES) could not detect any C or N, which indicates that the substrate does not have a significant amount of hydrocarbon impurity (within 0.01%).

Literature X-Ray Photoemission Spectroscopy (XPS) data for this product reports mainly Fe(III) with small amounts of Fe(II) and Fe(0), again suggesting hematite as the external surface of the substrate[1].

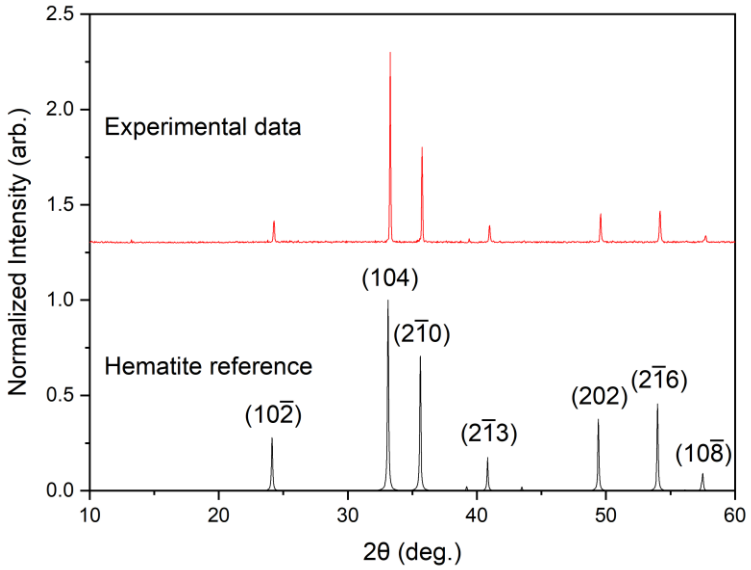

Figure S2. XRD pattern (black) of the powdered iron (III) oxide used as a substrate for adsorption isotherm experiments. A hematite reference (red) indicates good agreement. The data sets were normalized and offset in the *y* direction for clarity.

Deposited layer

Previous work in the group, conducted by Dr Mary H. Wood, has characterized silicon wafers with a deposited iron surface using XPS and XRD[2]. These were prepared in the same way as the substrates used in this work.

The XPS data show that the surface region of the film contains predominantly Fe(III), consistent with hematite, and a small amount of Fe(II), consistent with magnetite.

Similarly with the powdered iron oxide, the XRD pattern of the iron-deposited films is consistent with a literature hematite reference[2].

Attempt to determine molecular conformation using scanning tunneling microscopy (STM)

An STM study of 4NP on a single crystal of Fe_3O_4 was conducted in collaboration with Dr Colm Durkan at The Nanoscience Centre at the University of Cambridge. Figure S3 shows the bare substrate.

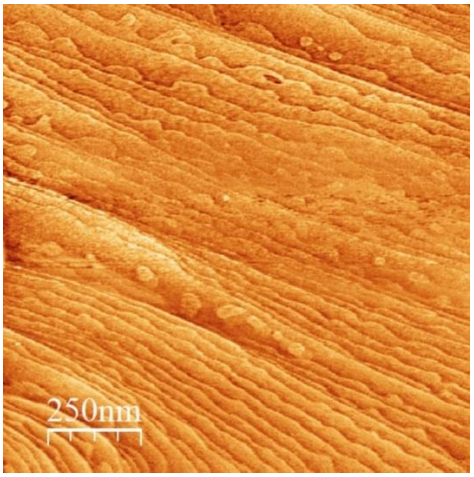

Figure S3. STM image of the bare surface of a single crystal of Fe_3O_4.

Figure S4 shows images of an iron oxide substrate that had been submerged in 4NP solution. The surface roughness increases from 0.6 to 0.85 nm and cross-sections show surface features between 0.6 to 1 nm tall and 1 nm wide. It is not possible to conclusively determine the molecular conformation of 4NP because the cantilever tip is of comparable size, resulting in a minimum measurable width of 1 nm.

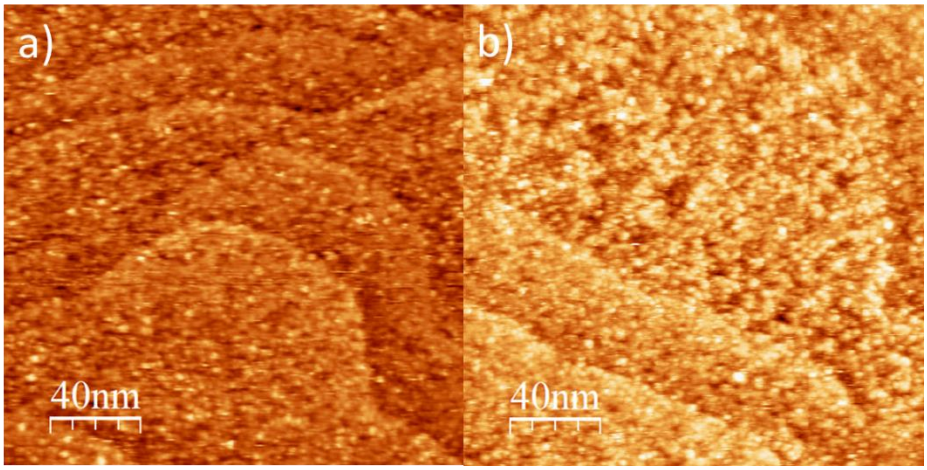

Figure S4. STM images of a bare single crystal of Fe_3O_4 before, a), and after, b), dipping in 4NP solution. Both have the same *z* scale.

4NP area estimations

Calculation of molecular sizes

4NP bulk density: 0.937 g cm^{-3} and relative molecular mass: 220.35 g mol^{-1}. Therefore, 4NP molecular volume: 391.9 $Å^3$ $molecule^{-1}$

Estimation of width, thickness and length 4NP

It is important to note that these calculations are only estimates of the molecular dimensions and are taken as indications only of the molecular orientation. We do not intend to use these to give a numerical value to the inclination angle.

a) Width
    a. The widest part is expected to be across the aromatic ring H-C-C-C-C-H. The bond lengths are 1.44 Å (C-C aromatic), 1.09 Å (C-H) and the van der Waals radii of H is approximately 1 Å. Therefore the total width is:

$$2(1 + 1.09\cos 30 + 1.44\cos 30) = 6.19\ Å$$

    b. The width of the alkyl chain is also of consideration. The bond lengths are 1.54 Å (C-C), 1.09 Å (C-H) and the van der Waals radii of H is approximately 1 $Å^3$. The bond angles are 109°. Therefore the total width is:

$$1.54\cos 54.5 + 2(1 + 1.09\cos 54.5) = 4.16\ Å$$

b) Thickness
    a. The thickness of the aromatic ring is approximately 3.36 Å, based on the interlayer spacing in graphite[4].
    b. The thickness of the alkyl chain, using previously defined bond lengths and angles, is:

$$2(1 + 1.09\cos 54.5) = 3.78\ Å$$

c) Length
    a. Additional bond lengths are 0.98 Å (OH) and 1.43 Å (CO) and additional bond angle for HOC is 104°. The length of the fully extended molecule is:

$$2 + 0.98\cos 38 + 1.43\cos 38 + 2(1.44\cos 30) + 9(1.54\sin 54.5) + 1.09\cos 35.5 = 18.56\ Å$$

d) Total volume
    a. Cross-section of aromatic part: $6.19 \times 3.36 = 20.80\ Å^2$
    b. Cross-section alkyl chain: $4.16 \times 3.78 = 15.70\ Å^2$
    c. Including length, considering aromatic cross-section: $20.8 \times 18.56 = 386.0\ Å^3$
    d. Including length, considering alkyl chain cross-section: $15.7 \times 18.56 = 291.4\ Å^3$
    e. A total volume of 386 $Å^3$ is consistent with the calculated molecular volume, hence we estimate dimensions of $(6.19 \times 3.36 \times 18.56)$ Å , as illustrated in Figure S5.

Maximum and minimum surface areas

Minimum surface area, described as 'upright' surface area, is: $6.19 \times 3.36 \sim \underline{21\ \text{Å}^2}$

Maximum surface area, described as 'flat' surface area, is: $6.19 \times 18.56 \sim \underline{115\ \text{Å}^2}$

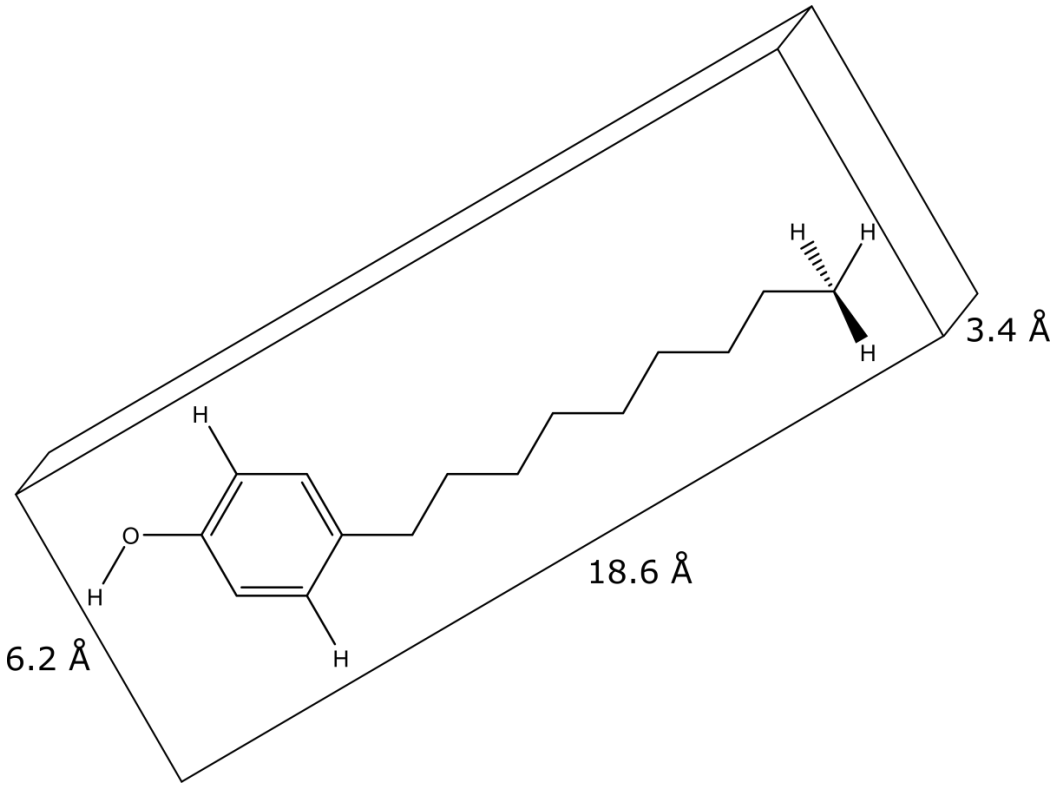

Figure S5. Schematic showing estimated dimensions of 4NP.

Carvacrol area estimations

Calculation of molecular sizes

Carvacrol bulk density: 0.976 g cm^{-3} and relative molecular mass: 150.22 g mol^{-1}. Therefore, carvacrol molecular volume: 255.6 $Å^3$ $molecule^{-1}$

It is important to note that these calculations are only estimates of the molecular dimensions and are taken as indications only of the molecular orientation. We do not intend to use these to give a numerical value to the inclination angle.

Estimation of width, thickness and length

a) Width
    a. The widest part is expected to be across the aromatic ring H-C-C-C-O-H. The bond lengths are 1.44 Å (C-C aromatic), 1.09 Å (C-H), 1.43 Å (C-O), 0.98 Å (O-H) and the van der Waals radii of H is approximately 1 $Å^3$. The bond angles are 120° in the benzene ring and 104° for the COH. Therefore the total width is:

$$2(1 + 1.44\cos 30) + 1.09\sin 60 + 1.43\sin 60 + 0.98\cos 38 = 7.45\ Å$$

b) Thickness
    a. The thickness of the alkyl chain, using previous bond lengths and angles, is:

$$2(1 + 1.09\cos 54.5) = 3.78\ Å$$

c) Length
    a. Additional bond angle for HCH is 109°. The length of the fully extended molecule is:

$$2(1 + 1.54 + 1.44\cos 60 + 1.09\cos 54.5) + 1.44 = 9.23\ Å$$

d) Total volume
    a. Cross-section: $7.45 \times 3.78 = 28.16\ Å^2$
    b. Volume: $9.23 \times 28.16 = 260.0\ Å^3$
    c. A total volume of 260 $Å^3$ is consistent with the calculated molecular volume, hence we estimate dimensions of $(7.45 \times 3.78 \times 9.23)$ Å , as illustrated in Figure S6.

Maximum and minimum surface areas

Minimum surface area, described as 'upright' surface area, is: $7.45 \times 3.78 \sim 28\ Å^2$

Maximum surface area, described as 'flat' surface area, is: $7.45 \times 9.23 \sim 69 Å^2$

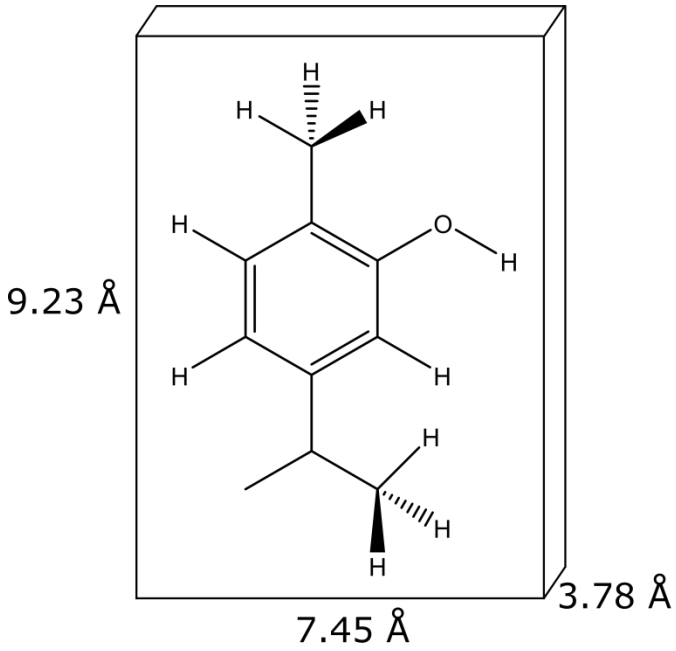

Figure S6. Schematic showing estimated dimensions of carvacrol.

Carvacrol SFG study

SFG spectra for carvacrol on iron oxide from d26-dodecane are presented in Figure S7 (b) and (c). The bulk FTIR spectrum is shown in Figure S7 (a).

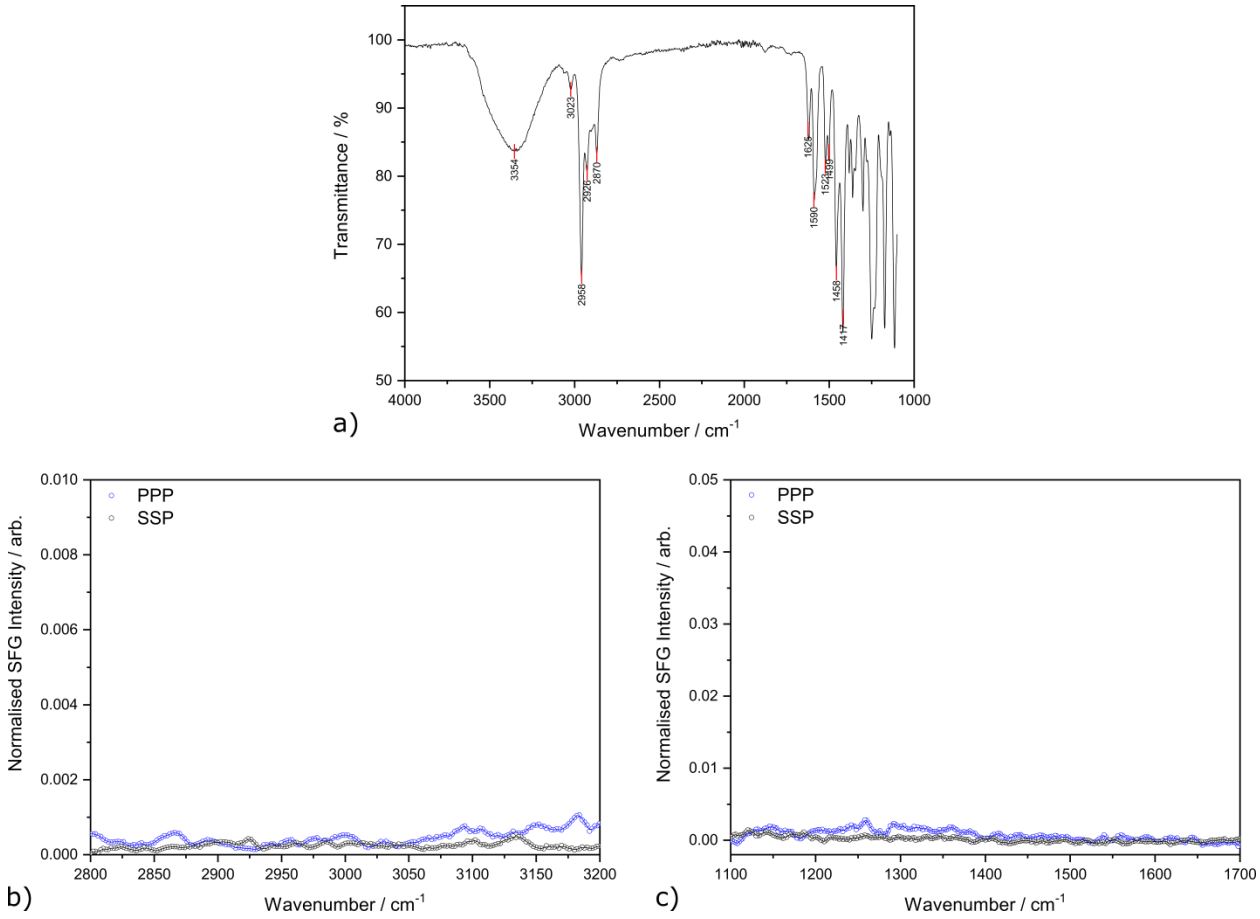

Figure S7. a) Bulk FTIR spectrum of carvacrol. b) SFG spectra of carvacrol on iron oxide from d26-dodecane in PPP (blue) and SSP (black) polarizations. c) SFG spectra of carvacrol on iron oxide from d26-dodecane in PPP (blue) and SSP (black) polarizations.

References

(1) Nikas, D. Characterization of Electrically Insulating Coatings for Soft Magnetic Composite Materials by Means of Surface Sensitive Analytical Techniques, Chalmers University of Technology, 2013.

(2) Wood, M. H. Adsorption at the Metal / Liquid Interface, University of Cambridge, 2015.

(3) Vogt, J.; Alvarez, S. Van Der Waals Radii of Noble Gases. *Inorg. Chem.* **2014**, *53* (17), 9260–9266.

(4) Kim, T.-H.; Jeon, E. K.; Ko, Y.; Jang, B. Y.; Kim, B.-S.; Song, H.-K. Enlarging the D-Spacing of Graphite and Polarizing Its Surface Charge for Driving Lithium Ions Fast. *J. Mater. Chem. A* **2014**, *2* (20), 7600–7605.