Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPORTING INFORMATION

Models for biomedical interfaces: computational study of quinone-functionalized amorphous silica surface features

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Computational details

Static calculations

Basis set. Considering the amorphous silica surface, Si atoms were represented by the 88-31G basis set of Nada et al. with $\alpha_{sp} = 0.1930$ bohr^{-2} as the most diffuse shell exponent and $\alpha_{pol} = 0.6100$ bohr^{-2} for polarization. O atoms were described by the 8-411G basis set of Nada et al. with $\alpha_{sp} = 0.1810$ bohr^{-2} as the most diffuse shell exponent and $\alpha_{pol} = 0.6000$ bohr^{-2}, while for H atoms we employed the 3-11G VTZP set of Ahlrichs et al. with $\alpha_{sp} = 0.1031$ bohr^{-2} as the most diffuse shell exponent and $\alpha_{pol} = 0.8000$ bohr^{-2}.

The atoms of the functionalizing quinone and of the allylamine were all described by the valence triple-zeta basis set with polarization (VTZP) of Ahlrichs et al.: a 511111-411G basis set for C, N and O (with $\alpha_p = 0.1008$ bohr^{-2} as the most diffuse shell exponent and $\alpha_{pol} = 0.8000$ bohr^{-2} for C, $\alpha_p = 0.1430$ bohr^{-2} as the most diffuse shell exponent and $\alpha_{pol} = 1.0000$ bohr^{-2} for N and with $\alpha_p = 0.1751$ bohr^{-2} as the most diffuse shell exponent and $\alpha_{pol} = 1.200$ bohr^{-2} for O). H atoms were represented with the same 3-11G VTZP set of Ahlrichs et al. used for the silica surface.

Computational parameters. The DFT exchange–correlation contribution was calculated with a numerical integration of the electronic density over a pruned grid of 75 radial points, with one sub-interval of 974 angular points. The Hamiltonian matrix was diagonalized over 4 k-points. The tolerances controlling the accuracy of the Coulomb and exchange series needed to build up the Fock matrix were set to 10^{-6} (ITOL1 = ITOL2 = 6). Tolerances for the maximum allowed gradient and the maximum atomic displacement for convergence were kept at the default values (0.00045 Ha·Bohr-1 and 0.00030 Bohr, respectively).

Amorphous silica model. The atomic fractionary coordinates of the amorphous silica surface are reported in the following input file for a CRYSTAL geometry optimization run. The label of the atomic layers for the partial optimization are indicated as well.

Amorphous silica surface coordinates (CRYSTAL input file)

```
SiO2 4.5 OH density, amorphous
SLAB
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12.60474583000 12.83351163000 83.131932
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0 3 1 0. 1.
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8 5
0 0 8 2.0 1.0
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      1.2266  0.0695
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      1.2340  0.3730   0.3542
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      0.4536  1.0      1.0
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      0.1810  1.0      1.0
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      0.60    1.0
1 4
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     1.1646626   0.20189726
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     0.10307241  1.0000000
0 2 1 0.0 1.0
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PBE
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XLGRID
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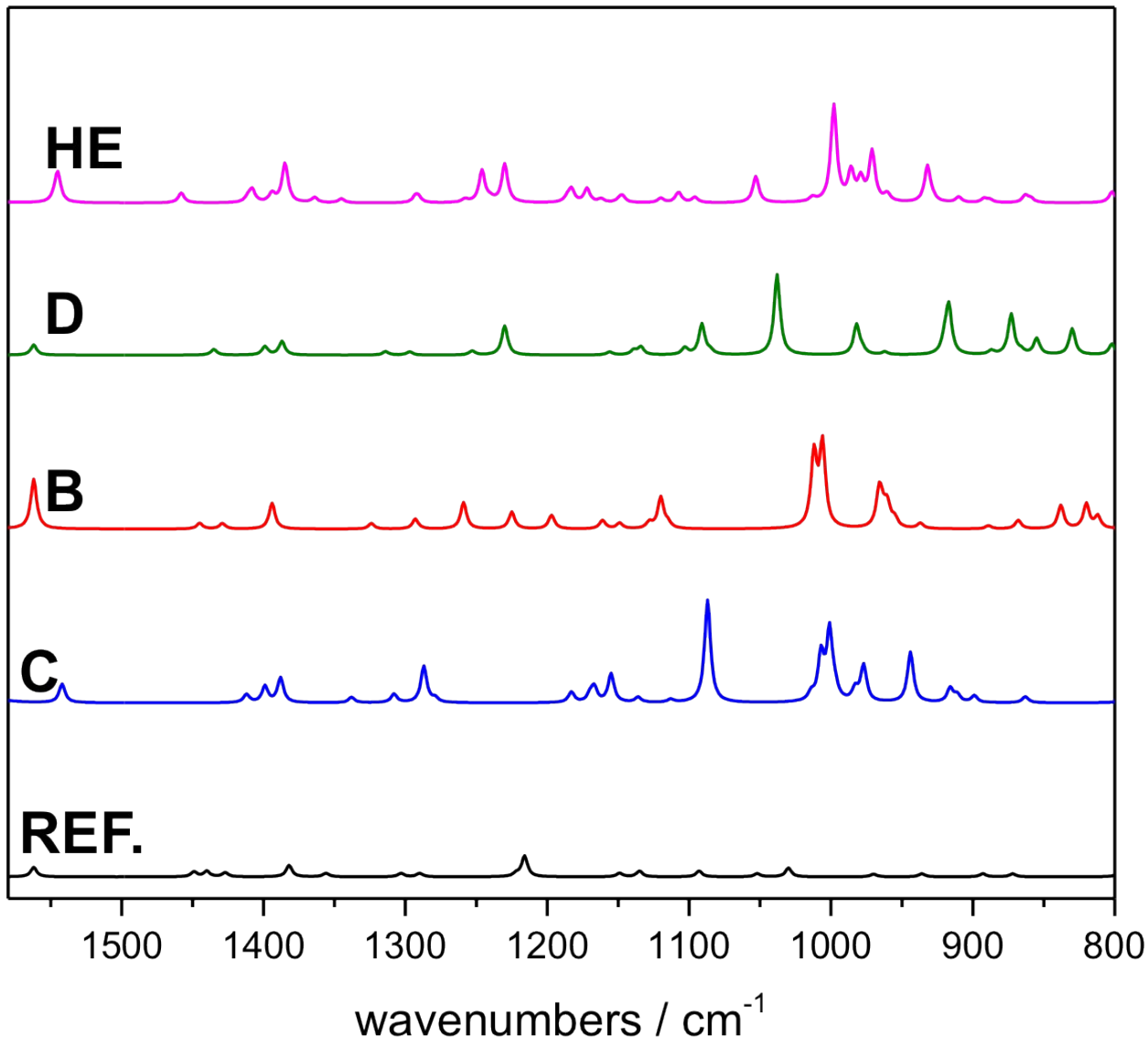
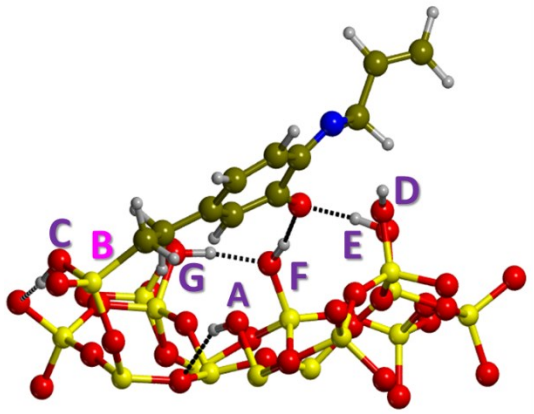


Figure ESI1. Complete computed IR spectra for the three mono-functionalized C, B and D models and for the bi-functionalized case HE, compared to the reference molecule, 4-ethyl-o-benzoquinone, displayed in Figure 1c) of the manuscript.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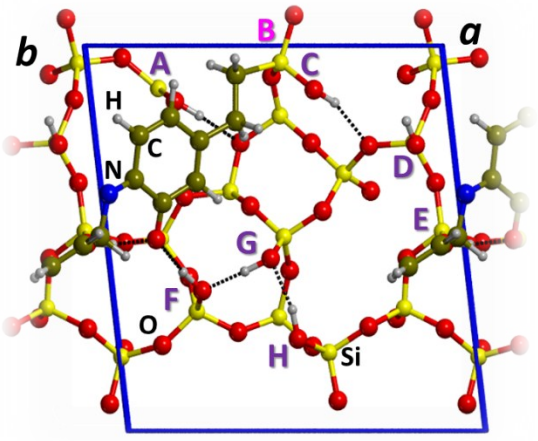
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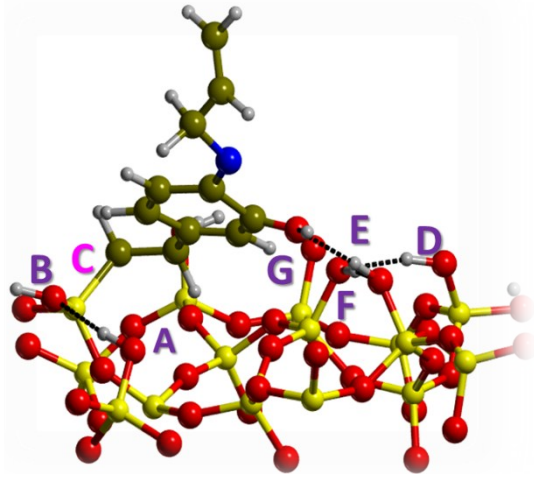
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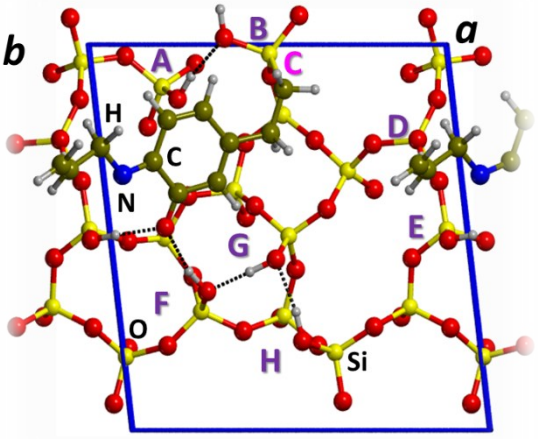
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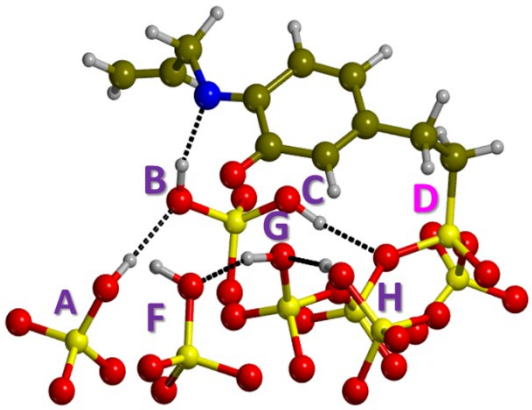
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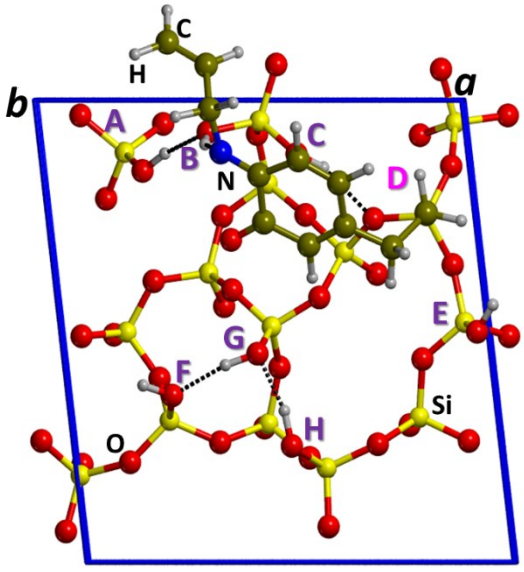
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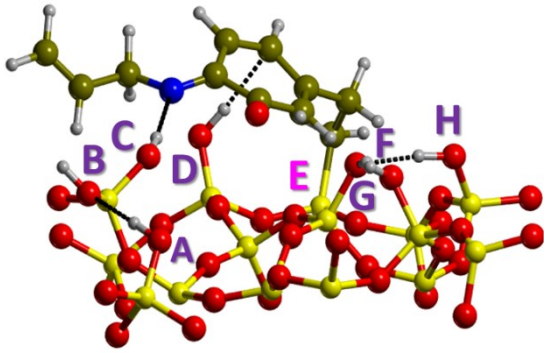
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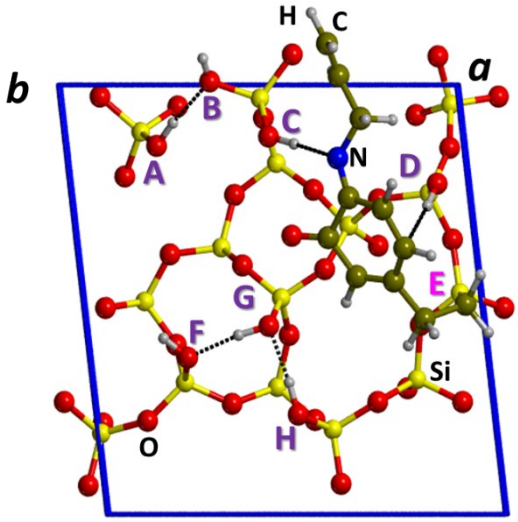
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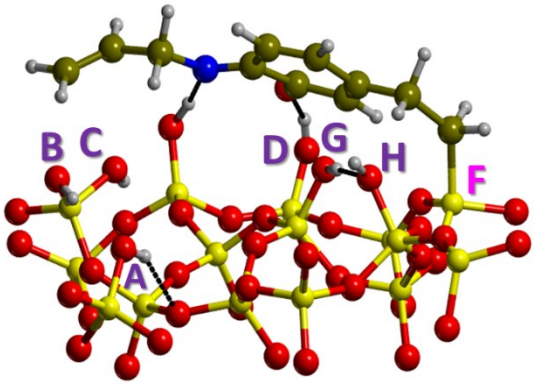
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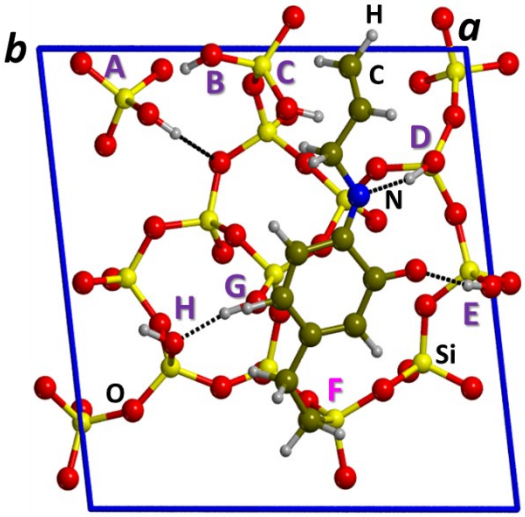
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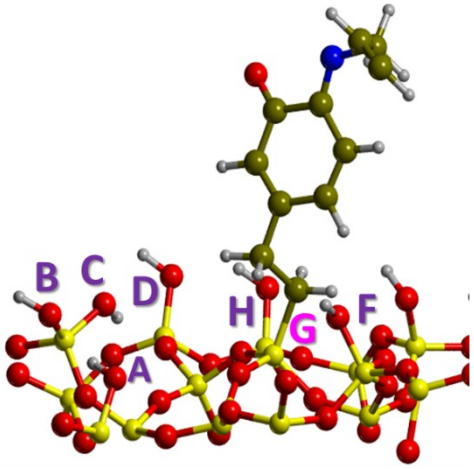
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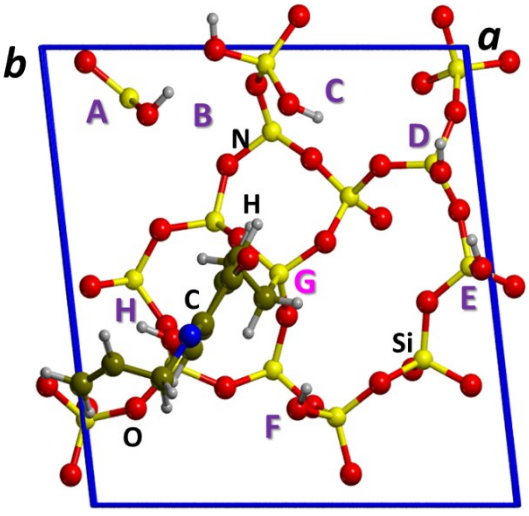
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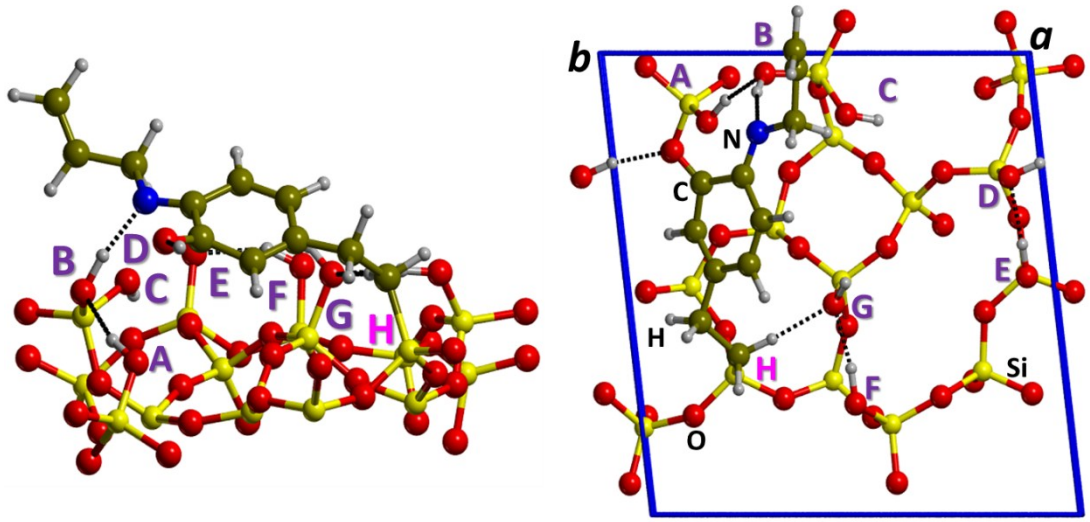

Figure ESI2. Side (left) and top (right) view of the imine products (see eq. 2) starting from different mono-functionalized models, labelled from B to H. Color code for atoms: silicon in yellow, oxygen in red, hydrogen in light grey, carbon in green, nitrogen in blue. H-bonds as black dotted lines; the label of the functionalized silanol in pink.