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# Electronic Supplementary Information for: Interface structure and reactivity of water-oxidation Ru-polyoxometalate catalysts on functionalized graphene electrodes.

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## 1 The Ru-POM/water interaction

The Lennard-Jones (LJ) parameters of Ru-POM and water employed in classical simulations are shown in Table SI-1. The LJ parameters for $O_{Ru}$ were assumed to be the same as the oxygen in the TIP3P water, while the LJ parameters for $O_{POM}$ were fitted to reproduce our QM/MM results[1]. We employed W parameters taken from the work of López et al.[2], for Si from the work of Tang *et. al*[3]. For the Ru-$O_{water}$ interaction we derived ad-hoc parameters, to correctly describe the bond-length between the Ru cations and their water ligands as shown in Fig. SI-1.

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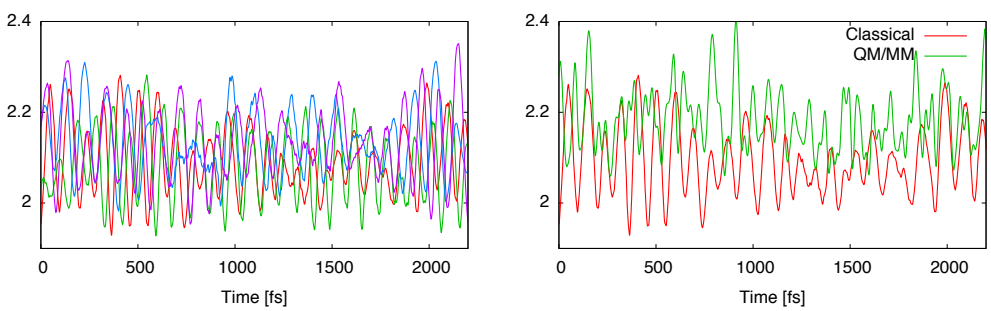
**Table SI-1** LJ parameters for rigid Ru-POM in TIP3P water

| Atoms | $\varepsilon$ (kcal/mol) | $\sigma$ (Å) | Charge |
|---|---|---|---|
| $O_{POM}$ | 0.1521 | 3.8000 | -0.912 |
| $O_{Ru}$ | 0.1521 | 3.1507 | -0.912 |
| H | 0.0000 | 0.0000 | 0.589 |
| W | 0.2211 | 2.3400 | 2.437 |
| Si | 0.4829 | 3.5800 | 1.821 |
| Ru | 0.0360 | 1.2040 | 1.883 |
| $O_{water}$ | 0.1521 | 3.1507 | -0.834 |
| $H_{water}$ | 0.0460 | 0.4000 | 0.417 |
| Ru - $O_{water}$ | 3.9000 | 1.9477 | |
| $Na^+$ | 0.0028 | 3.3284 | 1.000 |




**(a)** 4 Classical Ru-$O_{water}$ bond lengths **(b)** Ru-$O_{water}$ bond legth comparison

**Figure SI-1** Time evolution of four Ru-$O_{water}$ bond lengths in the classical simulation (a) and average Ru-$O_{water}$ bond length obtained in classical and QM/MM simulations (b)

## 2 Graphene/water interaction

The graphene substrate is modeled as a $(20 \times 30)$ single layer graphene sheet. We employ parameters from the literature[4,5] shown in Table SI-2 for the carbon atoms in graphene layer.

**Table SI-2** F.F. Parameters for graphene

| | | | | |
|---|---|---|---|---|
| Element | C | Mass 12.01 amu | Charge 0.0 | |
| Pair | C - C | $\varepsilon$ = 0.086 kcal mol$^{-1}$ | $\sigma$ = 3.400 Å | |
| Bond | C - C | $K_b$ = 478.4 kcal mol$^{-1}$ Å$^{-2}$ | $r_0$ = 1.42 Å | |
| Angles | C - C -C | $K_a$ = 67.2 kcal mol$^{-1}$ rad$^{-2}$ | $\theta_0$ = 120.0° | |
| Dihedral | - C - C - | $K_d$ = 3.625 | d = -1 | n = 2 |

# 3 Model system employed in DFT calculations

In the DFT-PBE calculations small planar benzene ring compounds, $C_{12}H_{24}$ (coronene) have been utilized to represent the single layer graphene as shown in Fig. SI-2.

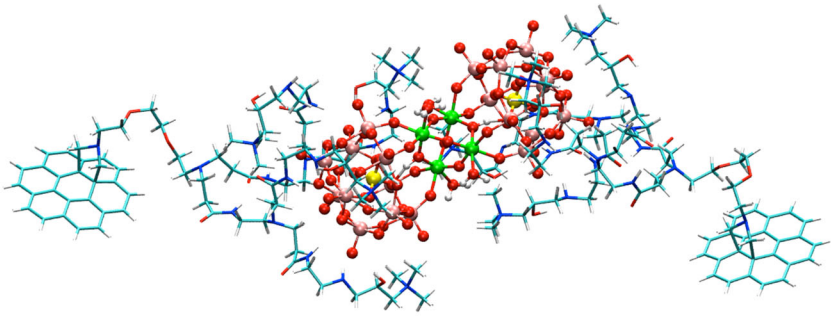


**Figure SI-2** Molecular structure of Ru-POM/dendrimer/graphene system studied using DFT. The graphene sheet is replaced by two coronene molecules.

# 4 Free energy profile

Information on the free energy profile for Ru-POM around the binding geometry in solution is shown in Fig. SI-3. The probability density $P(z)$ has been obtained from a histogram of the distance $z$ between the center of mass of Ru-POM and graphene, along the final

48 ns of molecular dynamics. $P(z)$ is normalized so that $\int_0^\infty P(z)dz = 1$. The free energy $F(z) = -k_B T \times log(P(z))$ has been shifted so that the minimum value is zero. The gaussian fit of the probability density, centered at 12.5 Å, has a standard deviation $\sigma = 1.6$ Å.

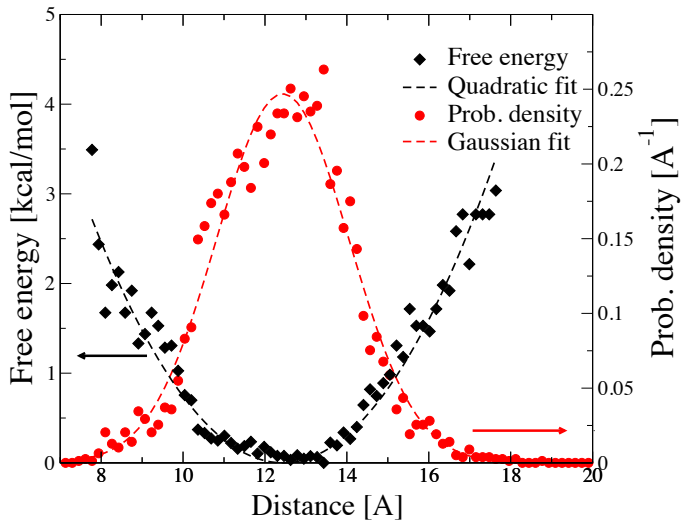



**Figure SI-3** Probability density and free energy profile as a function of the distance between the center of mass of Ru-POM and graphene, obtained from the last 48 ns of molecular dynamics at room temperature.

## References

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