**ELECTRONIC SUPPLEMENTARY INFORMATION**

**SURFACE ASSEMBLY OF PORPHYRIN NANORODS WITH ONE-DIMENSIONAL ZINC-OXYGEN SPINAL CORDS**

*Marta Trelka,[a] Christian Urban,[a] Celia Rogero,[b,c] Paula de Mendoza,[d] Eva Mateo-Marti,[b] Yang Wang,[e] Iñaki Silanes,[f,g] David Écija,[a] Manuel Alcamí,[e] Felix Yndurain,[a] Andrés Arnau,[c,f,h] Fernando Martín,[e,i] Antonio M. Echavarren,[d] José Ángel Martín-Gago,[b,j] José María Gallego,[i,j] Roberto Otero[a,i]* and Rodolfo Miranda[a,i]*

[a] *Dep. De Física de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Madrid, Spain. E-mail: roberto.otero@uam.es*
[b] *Centro de Astrobiología, CSIC-INTA, 28850, Madrid, Spain*
[c] *Centro de Fisica de Materiales CSIC-UPV/EHU, Materials Physics Center MPC, San Sebastian, Spain*
[d] *Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain*
[e] *Dep. de Química, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain.*
[f] *Donostia International Physics Center (DIPC), 20018 San Sebastian, Spain.*
[g] *Instituto de Hidráulica Industrial de Cantabria (IH), 39005 Santander, Spain*
[g]
[h] *Depto. Fisica de Materiales UPV/EHU, Facultad de Quimica, San Sebastian, Spain*
[i] *Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-NANO), Campus de Cantoblanco 28049 Madrid, Spain.*
[j] *Instituto de Ciencia de Materiales de Madrid –CSIC, Cantoblanco 28049 Madrid, Spain.*

## Synthesis of Zn-TMP

***meso*-Tetramesitylporphyrin (TMP)**.[Error! Bookmark not defined.] *General Lyndsey method for the synthesis of ortho-substituted tetraphenylporphyrins:* In a 1 L two-neck round-bottom flask with a septum and a reflux condenser, mesitylbenzaldehyde (0.74 mL, 5 mmol) and pyrrol (0.347 mL, 5 mmol) were added in dry $CHCl_3$ (300 mL). After the solution was purged with $N_2$ 5 min. 2.5 M $BF_3{\cdot}OEt_2$ (0.66 mL, 1.65 mmol) was added drop wise via syringe. After one hour, DDQ (0.922 g, 3.7 mmol) was added and the reaction was warmed at 61 ºC for an additional hour. The reaction mixture was cooled to room temperature and 1 equivalent of $Et_3N$ (0.23 mL, 1.6 mmol) was added and solvent was evaporated. The crude dry mixture was filtered through a column of $SiO_2$ (20 to 90 % $CH_2Cl_2$/hexane) and the purple solid was washed several times with methanol to give *meso*-tetramesitylporphyrin (245 mg, 25 %) as a purple solid. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.61 (s, 8H), 7.27 (s, 8H), 2.62 (s, 12H), 1.84 (s, 24H), -2.51 (s, 2H). MALDI positive observed 782.4 $[M]^+$ and $[M+H]^+$. IR (neat): n = 3317, 2916, 2848, 1469, 1375, 1345, 1212, 1189, 968, 945, 851, 825, 800, 733 $cm^{-1}$.

**Zinc *meso*-tetramesitylporphyrin (ZnTMP)**. In a round-bottom flask TMP (50 mg, 0.0639 mmol) and $Zn(OAc)_2$ (117 mg, 0.639 mmol) were added in a 3:1 $CH_2Cl_2$/MeOH (45/15 mL) solvent mixture and stirred at room temperature for 4 hours. Solvents were evaporated and the residue was chromatographed in neutral alumina (40 to 80 % $CHCl_3$/hexane) to give zinc-*meso*-tetramesitylporphyrin (42 mg, 78 %) as a pink solid.
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.68 (s, 8H), 7.26 (s, 8H), 2.62 (s, 12H), 1.84 (s, 24H). MALDI positive observed: $[M]^+$, $[M+H]^+$ and $2[M]^+$, $2[M+H]^+$. HRMS-CI m/z calcd for $C_{56}H_{52}N_4Zn$ $[M]^+$ 844.3476, found 844.3483. IR (neat): n = 2914, 2851, 1611, 1570, 1524, 1436, 1375, 1335, 1296, 1204, 1060, 998, 906, 852, 799, 723 $cm^{-1}$. UV ($CHCl_3$): $l_{max}$ = 421 (Soret), 550 nm.

## Theoretical Calculations

### *Calculations on finite porphyrin-ligand-porphyrin systems for different ligands*

Calculated binding energies for a number of possible ligands bridging a porphyrin dimer.

| MOL[a] | $E_{TOT}$[b] | DE[c] | **DE (BSSE)** | d_Zn...Zn[e] |
|---|---|---|---|---|

| | | | [d] | |
|---|---|---|---|---|
| porphyrin-monomer | -2435.4451833 | | | |
| $H_2O$ | -76.3209268 | | | |
| P-$H_2O$ | -2511.7876538 | -22.9 | **-13.5** | |
| P-$H_2O$-P | -4947.2331757 | -47.7 | **-13.7** | 4.45272 |
| $O_2$ | -150.1712813 | | | |
| P-$O_2$ | -2585.6163987 | -5.1 | **0.0** | |
| $CO_2$ | -188.3927244 | | | |
| P-$CO_2$-P | -5059.3054103 | -25.0 | **-14.0** | 6.70112 |
| CO | -113.1826101 | | | |
| P-CO-P | -4984.0814631 | -24.1 | **-5.3** | 6.0587 |
| FA | -189.5525717 | | | |
| P-FA-P | -5060.4604344 | -36.4 | **-11.0** | 5.60439 |

[a]

Notations 'P' for porphyrin, 'FA' for formic acid.

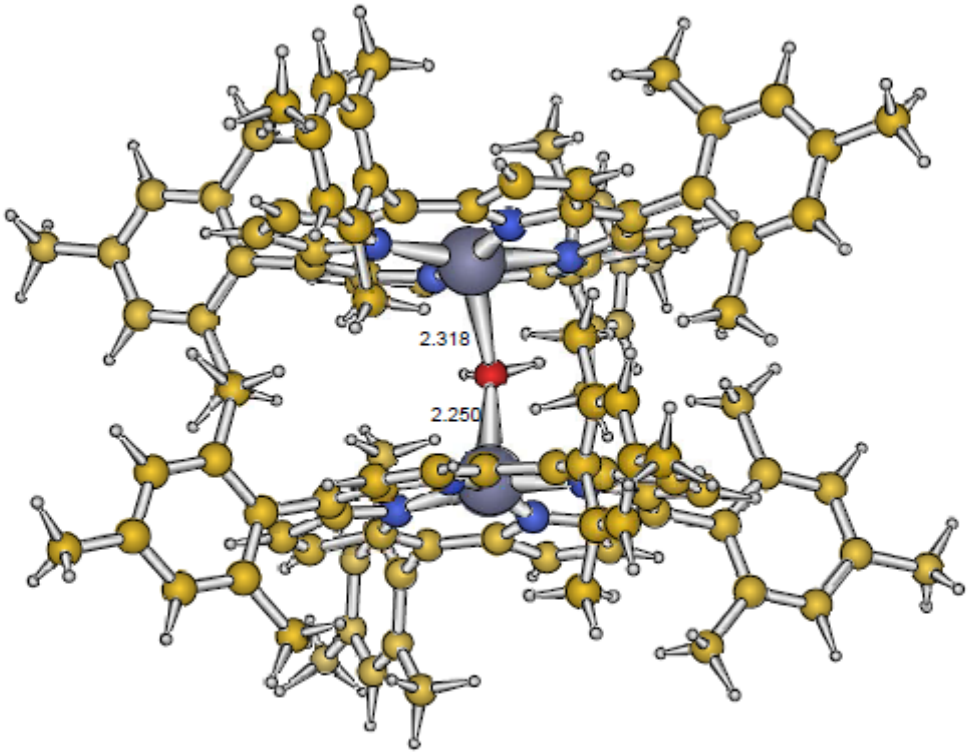
[b] Total DFT energy (a.u.).

[c] Binding energy (kcal/mol) without BSSE correction.

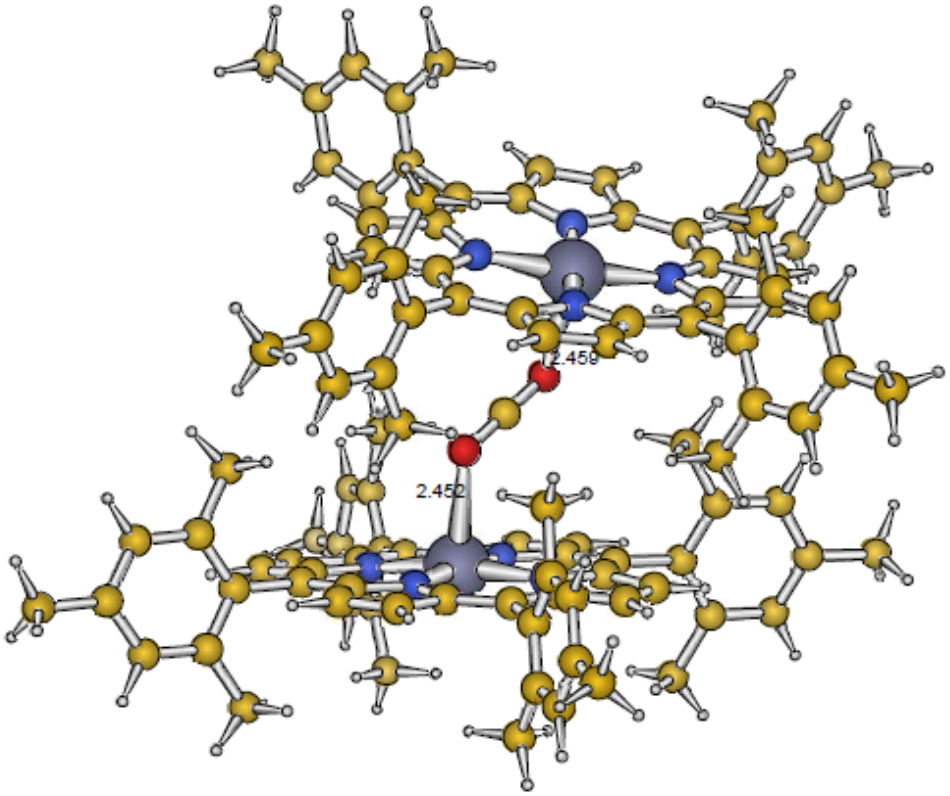
[d] Binding energy (kcal/mol) including BSSE correction.

[e] Zn...Zn distance (Å).

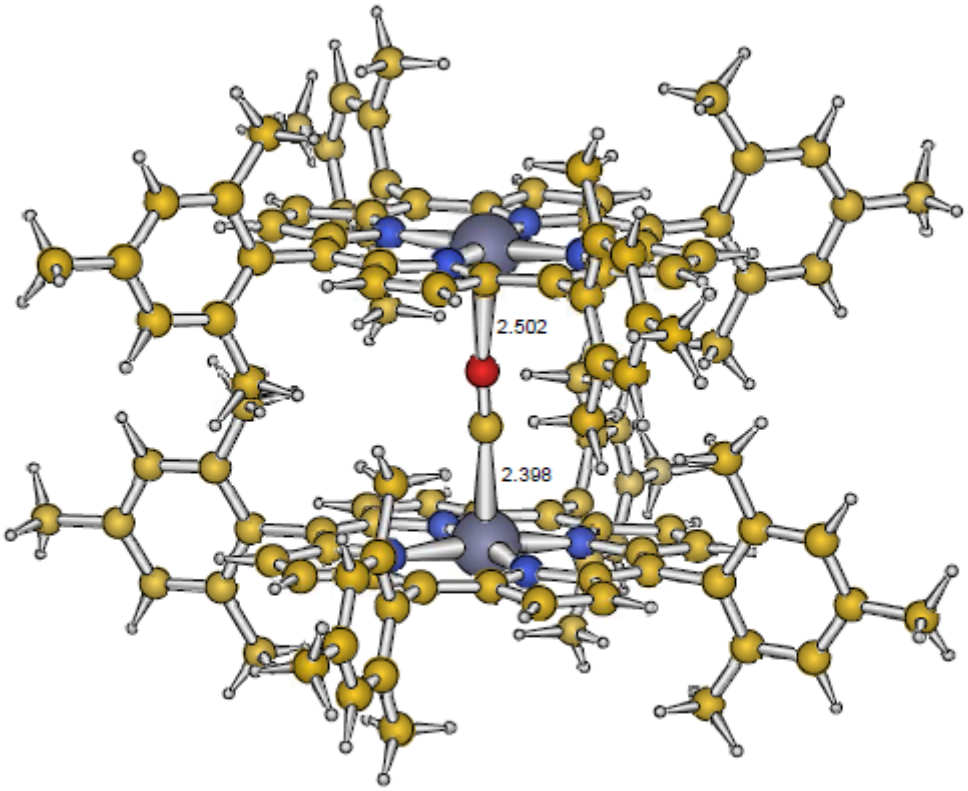
The relaxed geometry for each ligand is shown below



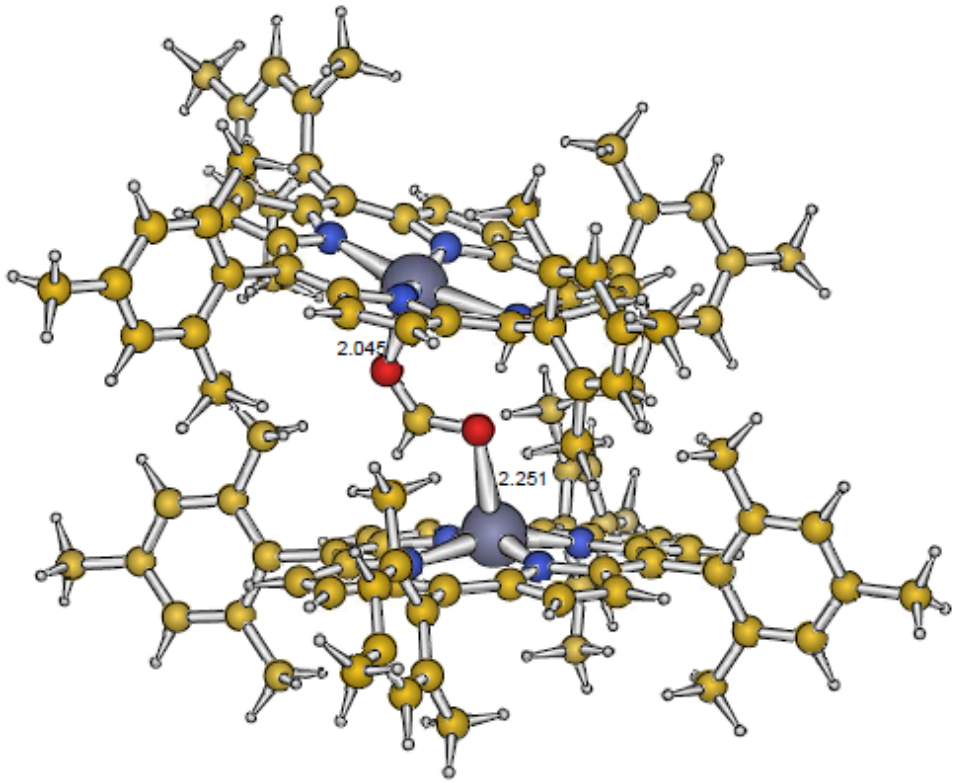

P-$H_2O$-P




P-$CO_2$-P




P-CO-P




P-FA-P

***Calculations on periodic porphyrin-ligand-porphyrin systems for different ligands***

No ligand

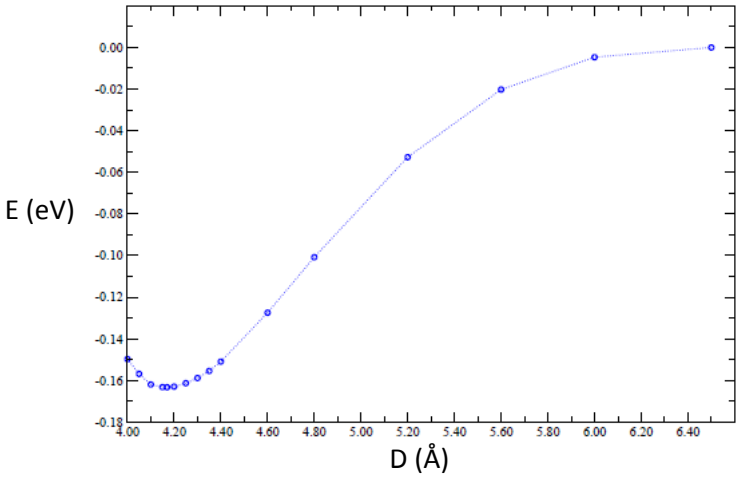
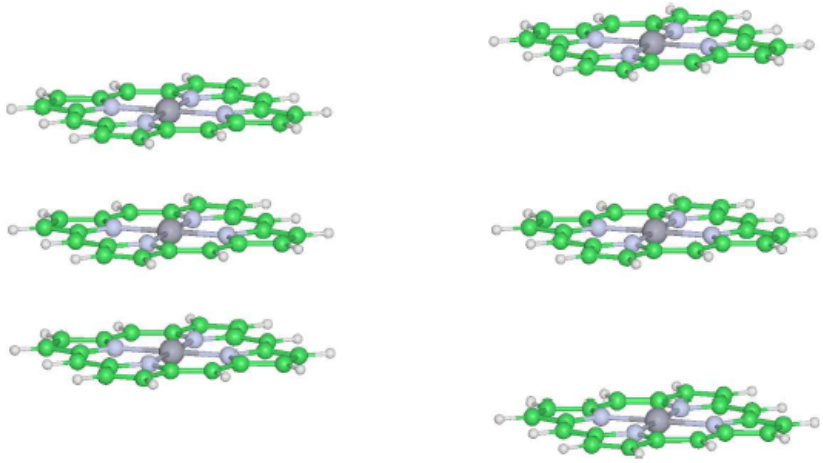


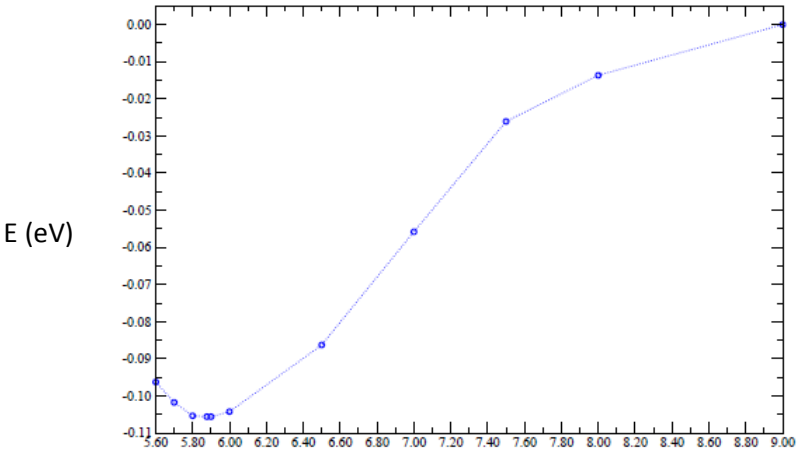

Figure 1: E vs. $d_0$ for ZnPor. Distance in Å, energy in eV.

Geometry

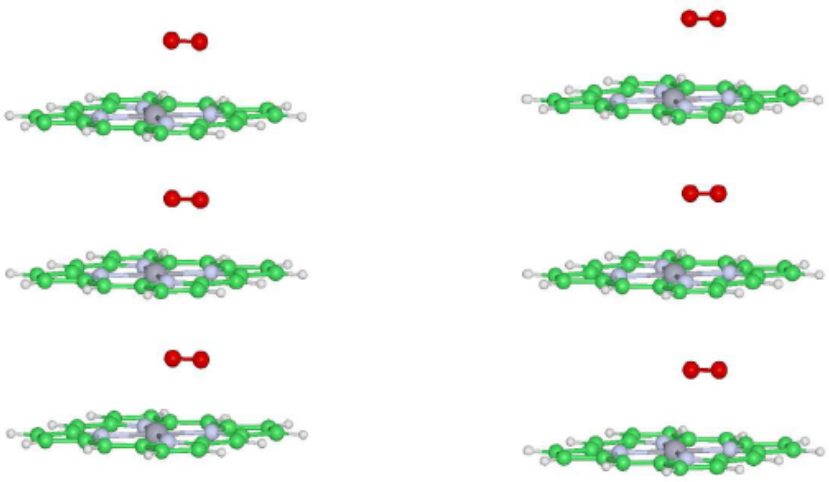


Optimal geometry ($d_0$ = 4.17 Å) Geometry for $d_0$ = 6.50 Å

Molecular oxygen

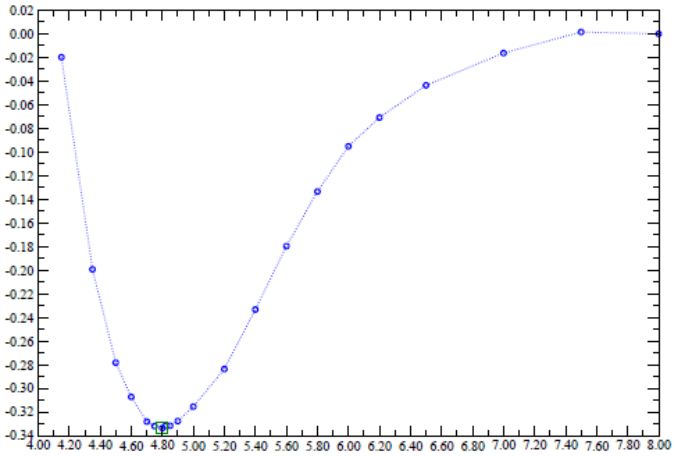



Geometry

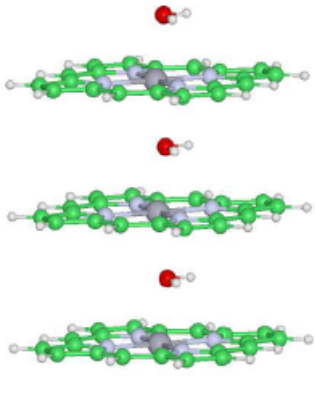


Optimal geometry ($d_0$ = 5.88 Å) Geometry for $d_0$ = 6.50 Å

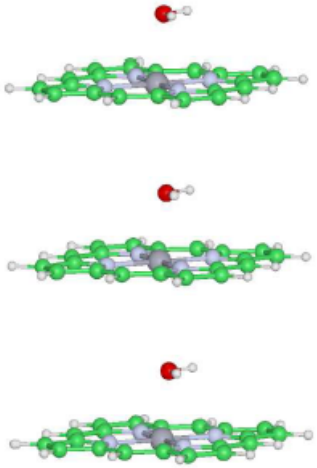
## Water




Geometry



Optimal geometry ($d_0 = 4.82$ Å)



Geometry for $d_0 = 6.50$ Å