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

Ab Initio Molecular Dynamics Study of the Coordination properties of metal chelator Clioquinol to Zn^{2+}

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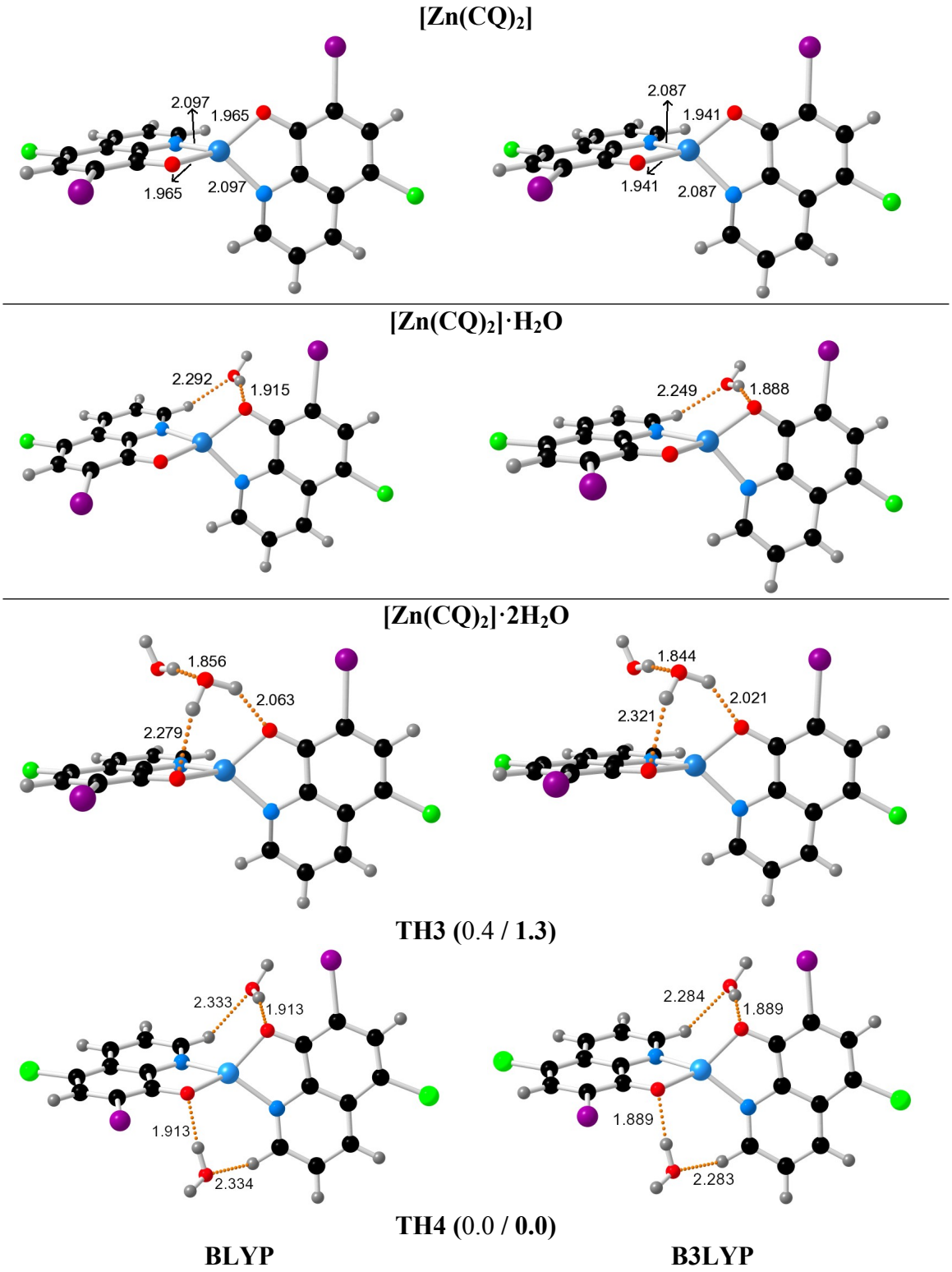


Figure S1. BLYP and B3LYP gas phase optimized geometries of $[Zn(CQ)_2]\cdot nH_2O$ complexes with n = 0, 1 and 2. Distances are in Å. For complexes with more than one isomer, relative free energies in kcal mol^{-1} at the BLYP / **B3LYP** levels are given in parenthesis.

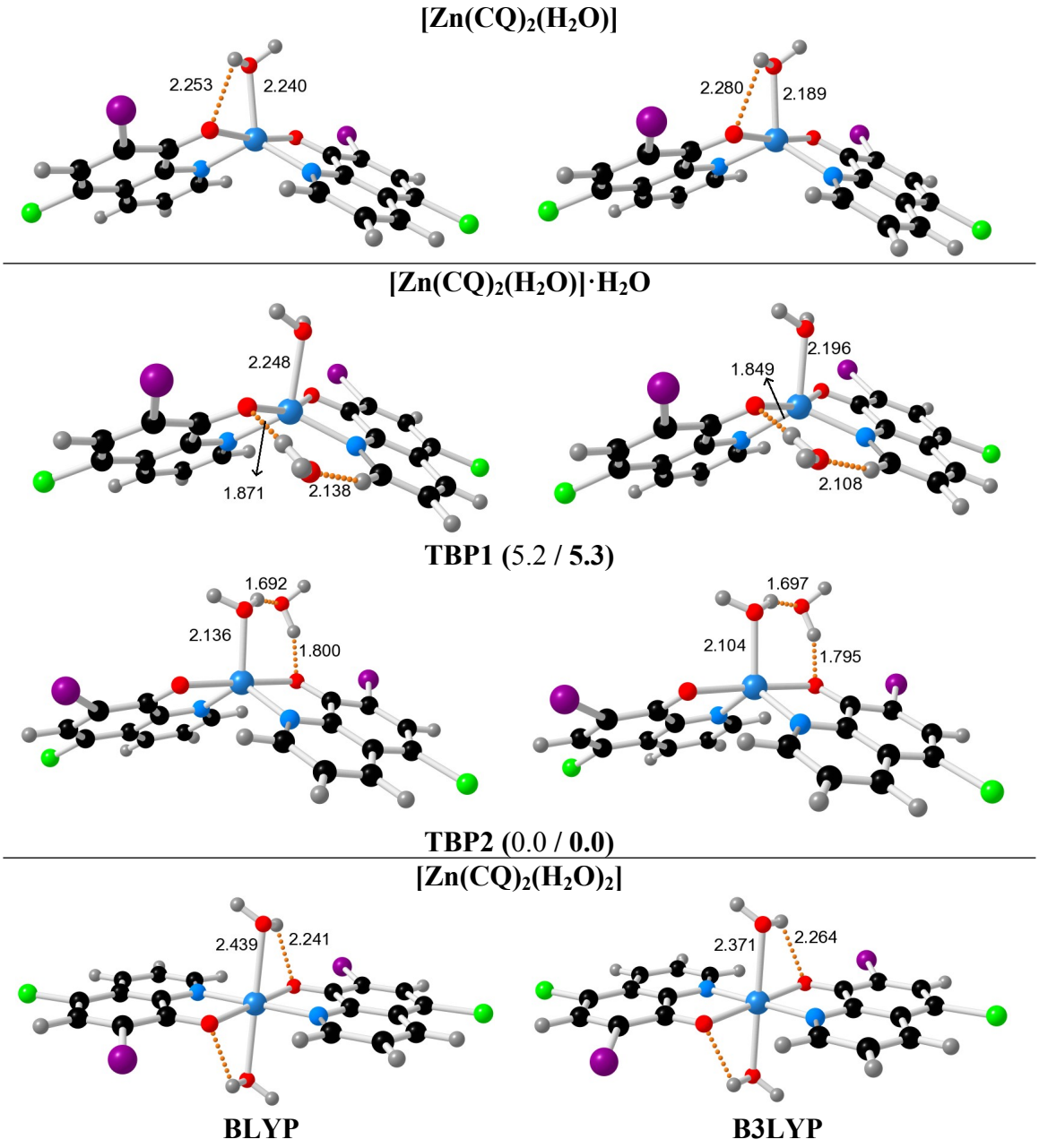


Figure S2. BLYP and B3LYP gas phase optimized geometries of $[Zn(CQ)_2(H_2O)]\cdot nH_2O$ with n = 0, 1 and $[Zn(CQ)_2(H_2O)_2]$ complexes. Distances are in Å. For complexes with more than one isomer, relative free energies in kcal mol^{-1} at the BLYP / **B3LYP** levels are given in parenthesis.

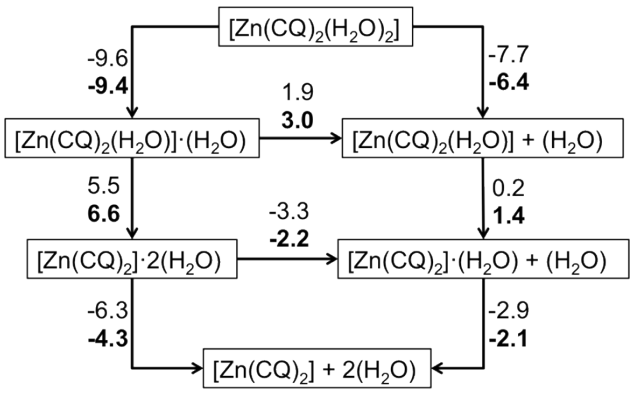
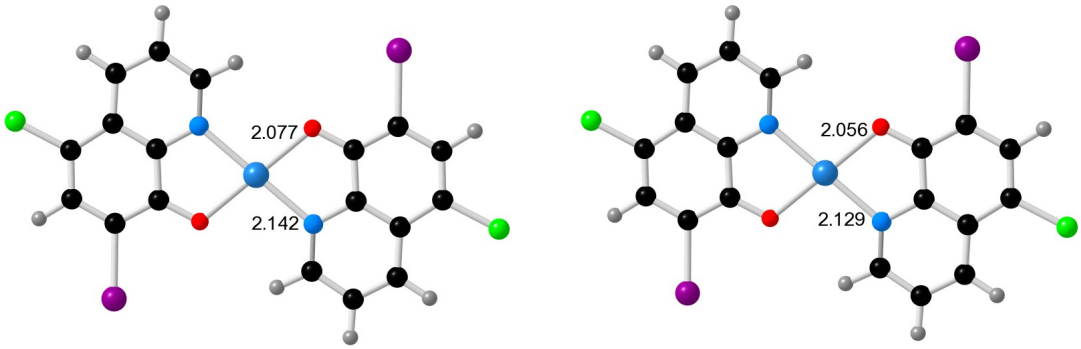
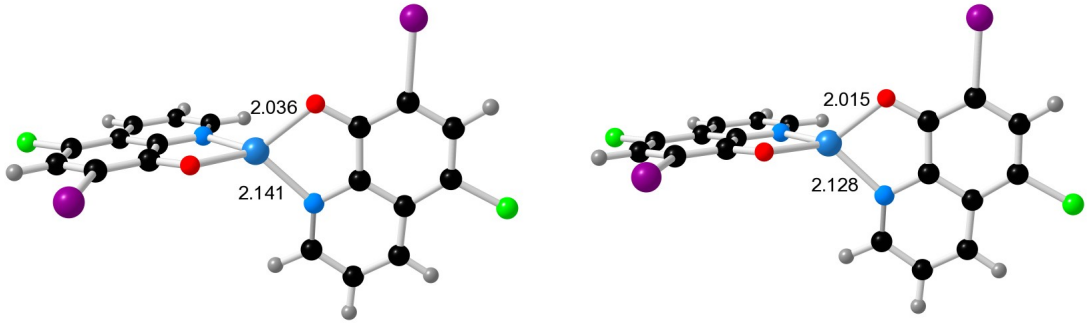


Figure S3. BLYP and **B3LYP** (in bold) gas phase reaction free energies (ΔG^0_{gas}, in kcal/mol) for the different steps involved in the dissociation of the two water molecules of $[Zn(CQ)_2(H_2O)_2]$.

[Zn(CQ)$_2$]

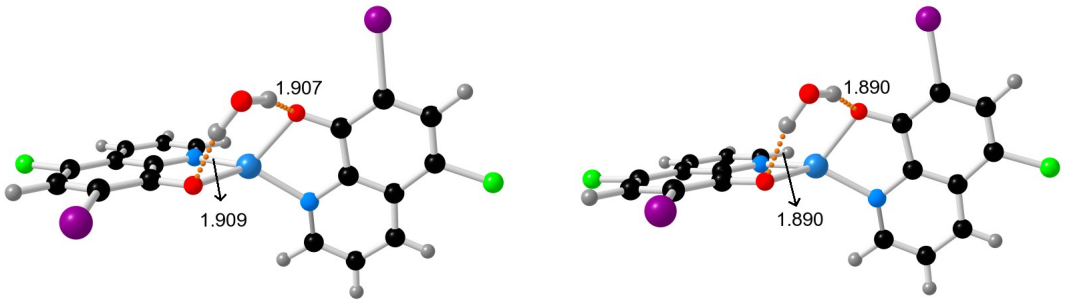


SQP (4.4 / **4.1**)

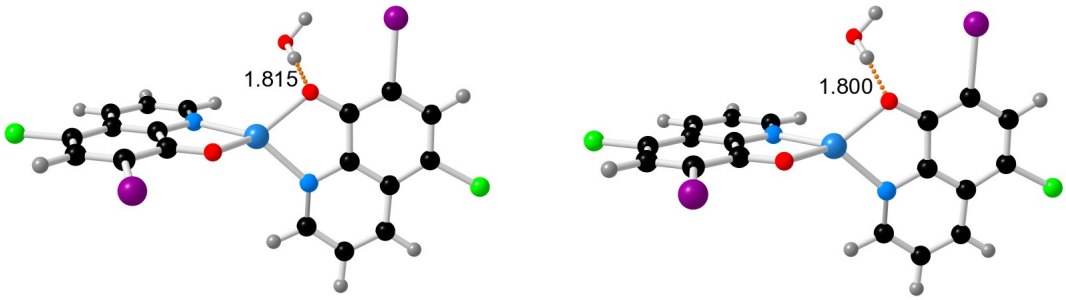


TH (0.0 / **0.0**)

[Zn(CQ)$_2$]·H$_2$O

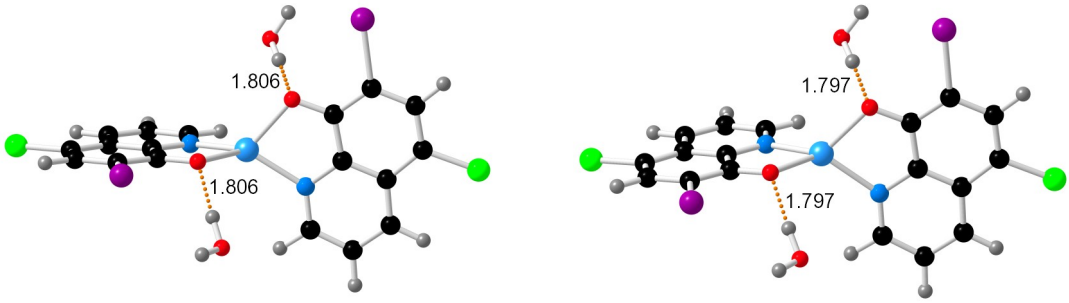


TH2 (0.8 / **0.8**)

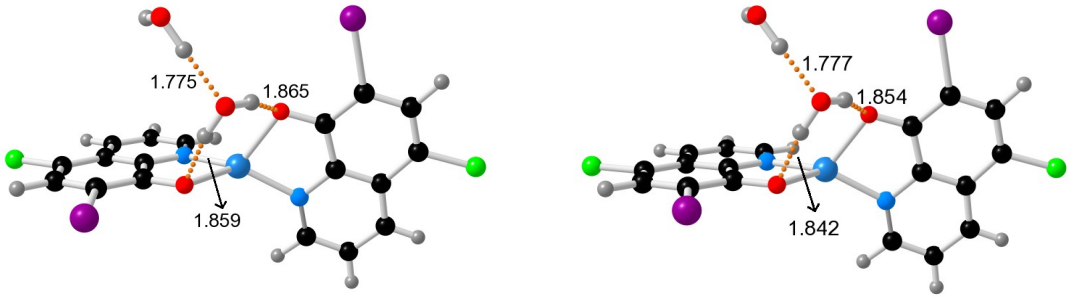


TH1 (0.0 / **0.0**)

[Zn(CQ)$_2$]·2H$_2$O



TH4 (2.1 / **0.0**)

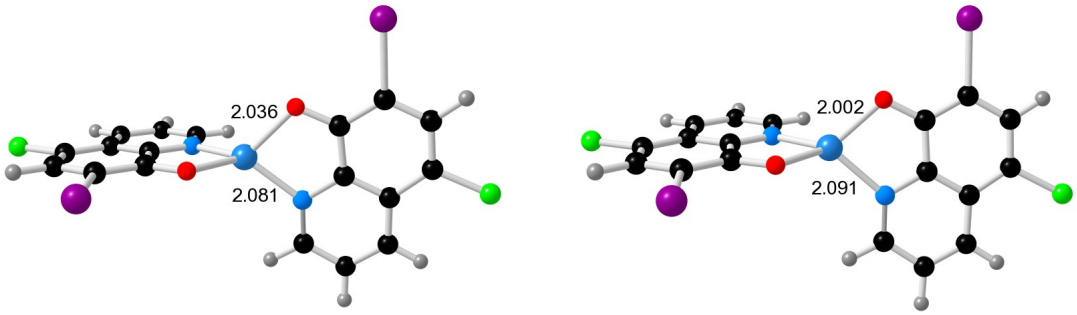


TH3 (0.0 / **0.0)**

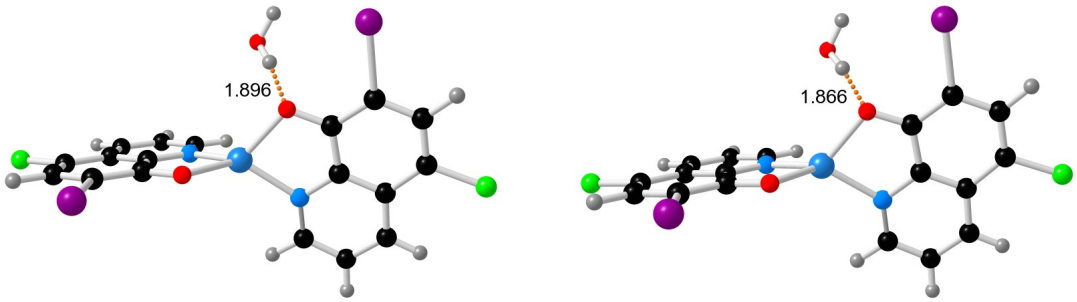
BLYP **B3LYP**

Figure S4. BLYP and B3LYP solution phase (SMD method) optimized geometries of $[Zn(CQ)_2]\cdot nH_2O$ complexes with n = 0, 1 and 2. Distances are in Å. For complexes with more than one isomer, relative free energies in kcal mol^{-1} at the BLYP / **B3LYP** levels are given in parenthesis.

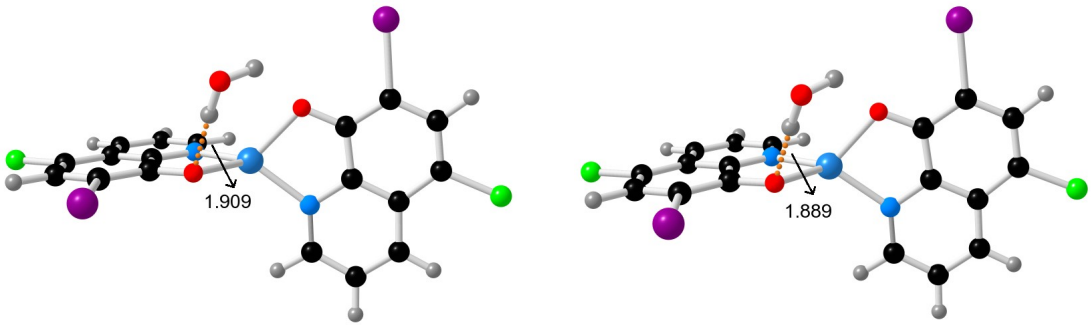
[Zn(CQ)$_2$]



[Zn(CQ)$_2$]·H$_2$O

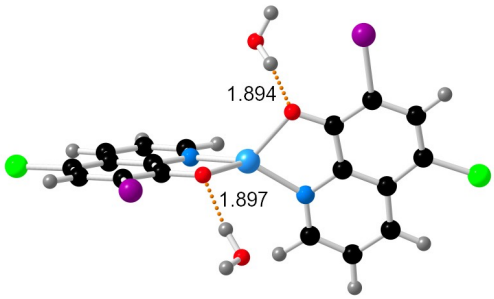


TH1 (0.3 / **1.3**)

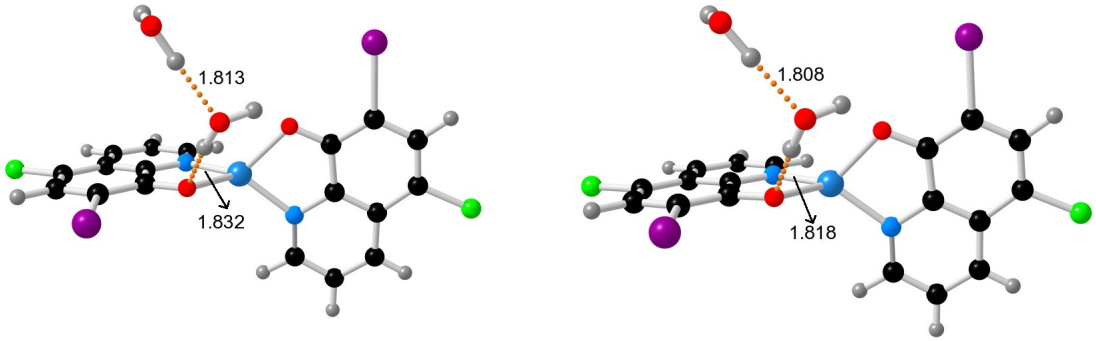


TH2 (0.0 / **0.0**)

[Zn(CQ)$_2$]·2H$_2$O



TH4 (0.4 / **0.0**)

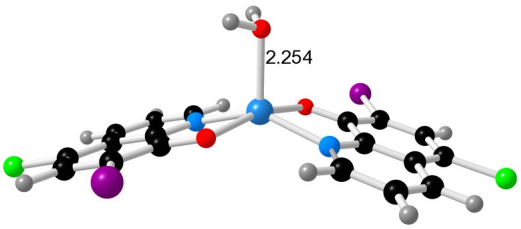


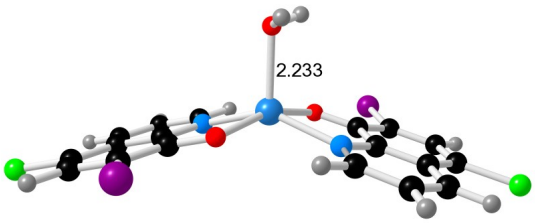
TH3 (0.0 / **0.0**)

BLYP **B3LYP**

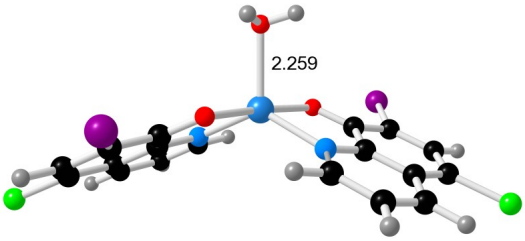
Figure S5. BLYP and B3LYP solution phase (CPCM method) optimized geometries of $[Zn(CQ)_2]\cdot nH_2O$ complexes with n = 0, 1 and 2. Distances are in Å. For complexes with more than one isomer, relative free energies in kcal mol^{-1} at the BLYP / **B3LYP** levels are given in parenthesis

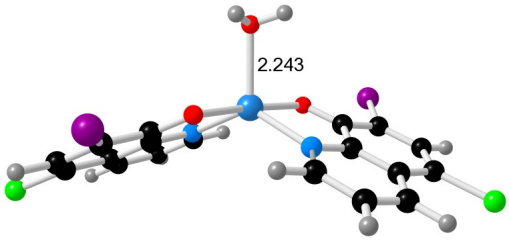
[Zn(CQ)$_2$(H$_2$O)]



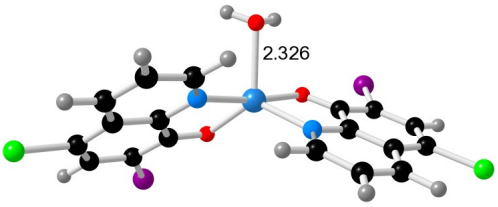


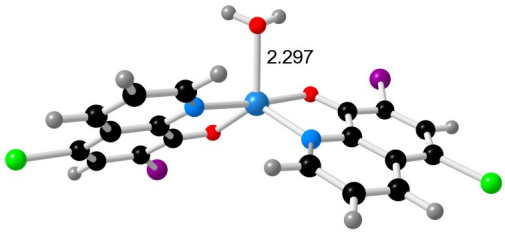
SBP (0.9 / **0.7**)



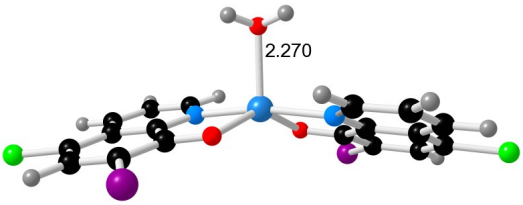


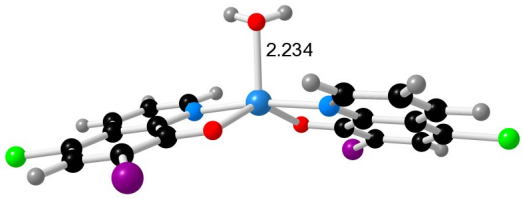
TBPoo (0.1 / **0.5**)





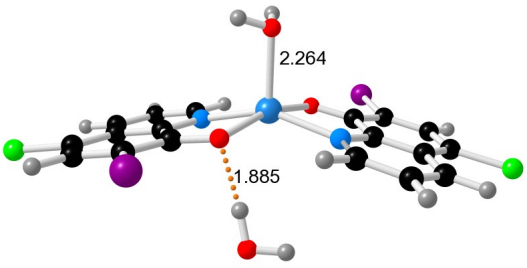
TBPno (0.0 / **0.0**)

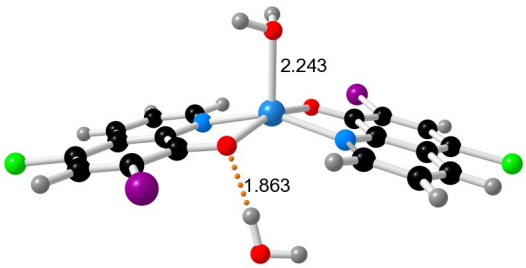




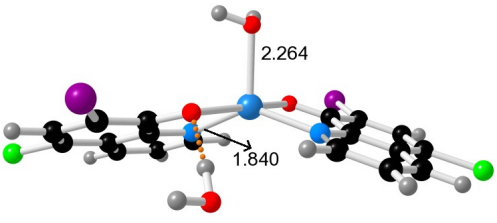
TBPnn (0.4 / **1.3**)

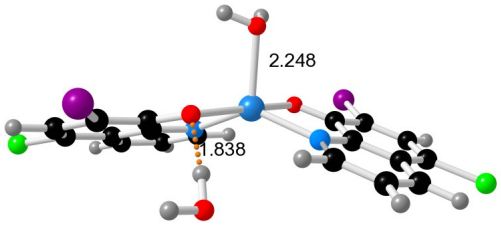
[Zn(CQ)$_2$(H$_2$O)]·H$_2$O



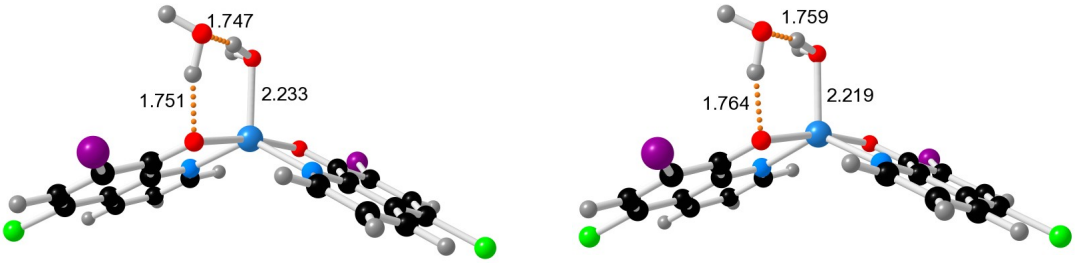


SBP (1.8 / **0.8**)





TBPoo1 (1.7 / **1.4**)

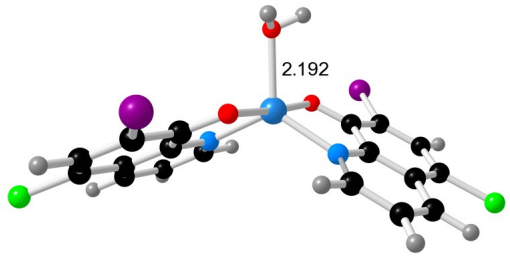


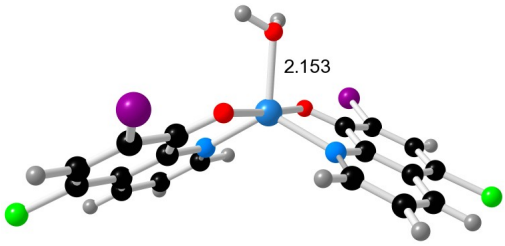
TBPoo2 (0.0 / **0.0)**

BLYP **B3LYP**

Figure S6. BLYP and B3LYP solution phase (SMD method) optimized geometries of $[Zn(CQ)_2(H_2O)]\cdot nH_2O$ complexes with n = 0 and 1. Distances are in Å. For complexes with more than one isomer, relative free energies in kcal mol^{-1} at the BLYP / **B3LYP** levels are given in parenthesis**.**

[Zn(CQ)$_2$(H$_2$O)]





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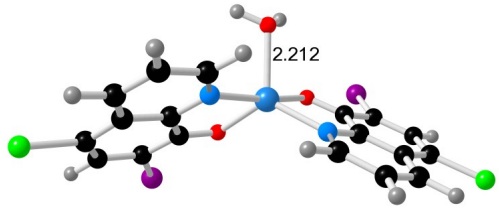
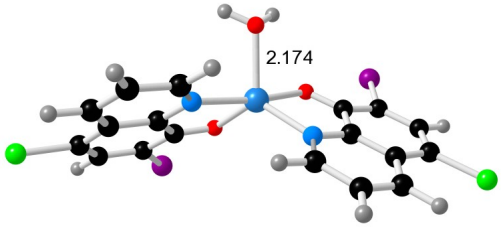
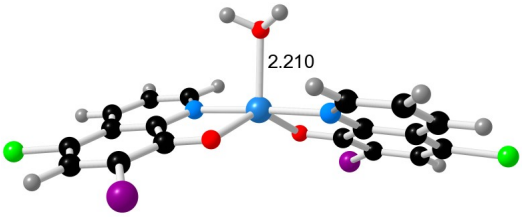
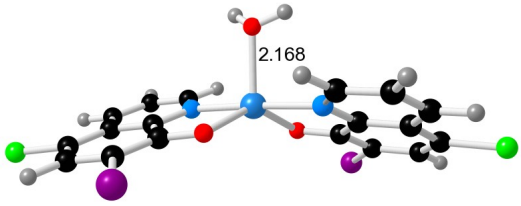




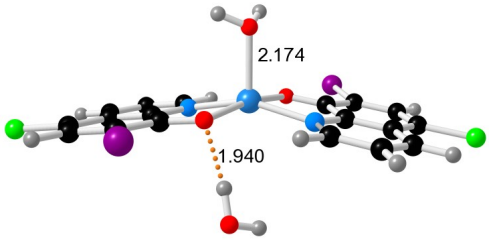
TBPno (0.2 / **0.9**)



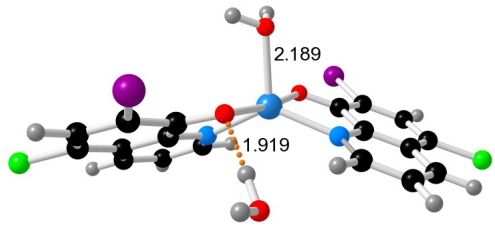


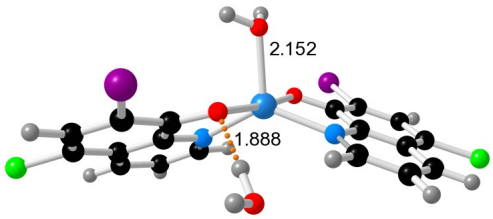
TBPnn (0.0 / **0.0**)

[Zn(CQ)$_2$(H$_2$O)]·H$_2$O

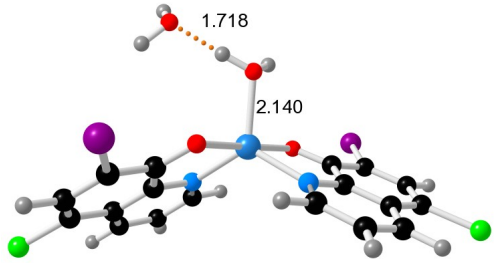


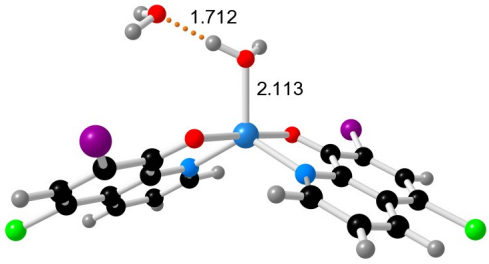
SBP (**--**/ **3.4**)





TBPoo1 (5.0 / **4.5**)



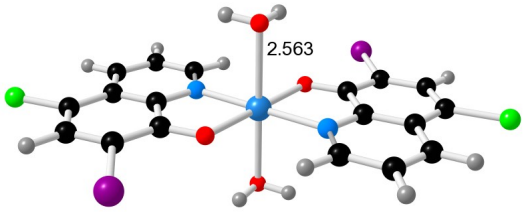


TBPoo2 (0.0 / **0.0**)

BLYP **B3LYP**

Figure S7. BLYP and B3LYP solution phase (CPCM method) optimized geometries of [Zn(CQ)$_2$(H$_2$O)]·nH$_2$O complexes with n = 0 and 1. Distances are in Å. For complexes with more than one isomer, relative free energies in kcal mol^{-1} at the BLYP / **B3LYP**

[Zn(CQ)$_2$(H$_2$O)$_2$]



BLYP **B3LYP**

Figure S8. BLYP and B3LYP solution phase (SMD method) optimized geometries of [Zn(CQ)$_2$(H$_2$O)$_2$] complex. Distances are in Å.

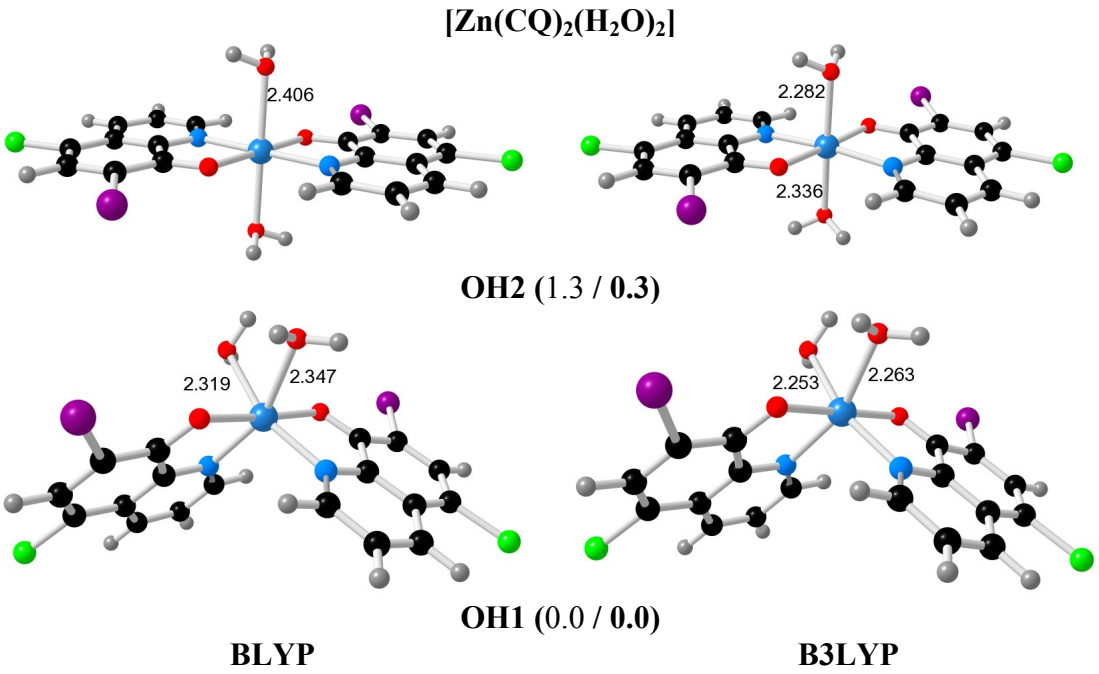


Figure S9. BLYP and B3LYP solution phase (CPCM method) optimized geometries of $[Zn(CQ)_2(H_2O)_2]$ complex. Distances are in Å. Relative free energies in kcal mol^{-1} at the BLYP / **B3LYP** levels are given in parenthesis**.**

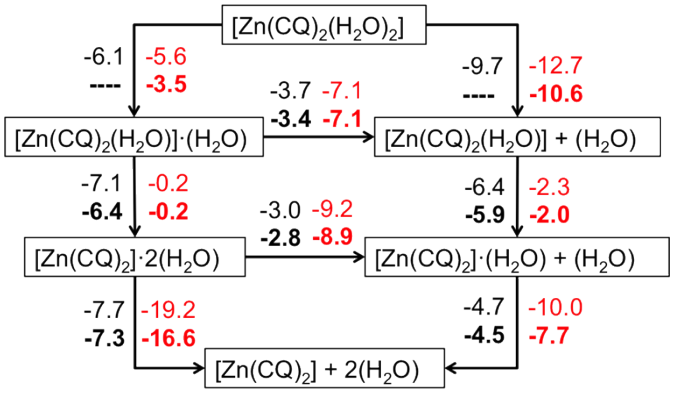


Figure S10. BLYP and **B3LYP** (in bold) SMD solution phase reaction free energies (ΔG^*_{sol}, in kcal/mol) for the different steps involved in the dissociation of the two water molecules of $[Zn(CQ)_2(H_2O)_2]$. Values using CPCM method are shown in red.

Explicit solvent simulations.

The structure of water was analyzed to confirm the proper behavior of the simulations. Figure S11 shows the radial distribution functions (RDF) of water and Table S1 summarizes the different parameters associated to the first peak of both simulations along with the recommended values reported by Skinner et al.[1] in a recent benchmark X-ray diffraction study of the RDF of water. It can be observed that the obtained values are in good agreement with the experimental data indicating that the models show the expected bulk solvent behavior.

Table S1. Position and intensity of the first peak and coordination number of the O_w-O_w radial distribution function.

	Simulation A	**Simulation B**	**x-ray[a]**
r1 (Å)	2.81	2.79	2.80(1)
g(O_w-O_w)	2.59	2.59	2.57(5)
CN(O_w-O_w)	4.6	4.9	4.3(1)

[a] Reference [1].

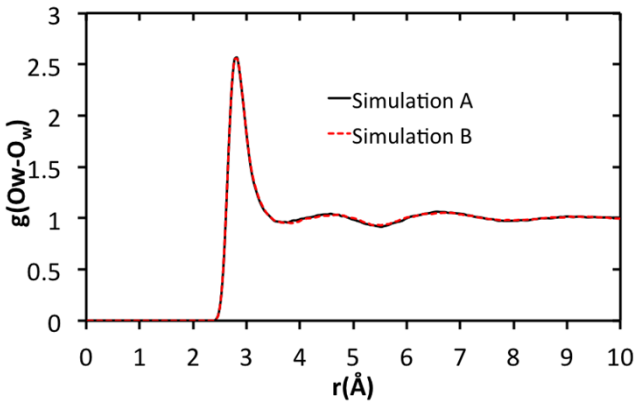


Figure S11. Radial distribution of water oxygen atoms (O_w-O_w) around $[Zn(CQ)_2H_2O]$ (simulation A) and $[Zn(CQ)_2]$ (simulation B)

References

(1) Skinner, L. B.; Huang, C.; Schlesinger, D.; Pettersson, L. G. M.; Nilsson, A.; Benmore, C. J. Benchmark Oxygen-Oxygen Pair-Distribution Function of Ambient Water from X-Ray Diffraction Measurements with a Wide Q-Range. *J. Chem. Phys.* **2013**, *138*, 074506.