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*Supporting information*

# Tetranuclear oxo-titanium clusters with different aromatic ligands: optical properties, DFT calculations, and photoactivity

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**Table S1.** Comparison of the experimental and the calculated (DFT) structural data of $\{Ti_4O_2\}$ cores of studied oxo-clusters: $[Ti_4O_2(O^iBu)_{10}(O_2CC_{13}H_9)_2]$ (**1**), $[Ti_4O_2(O^iBu)_{10}(O_2CC_6H_4Cl)_2]$ (**2**), $[Ti_4O_2(O^iBu)_{10}(O_2CC_6H_4NO_2)_2]$ (**3**),. $[Ti_4O_2(OMe)_{10}(O_2CC_{13}H_9)_2]$ DFT(**1**), $[Ti_4O_2(OMe)_{10}(O_2CC_6H_4Cl)_2]$ DFT(**2**), $[Ti_4O_2(OMe)_{10}(O_2CC_6H_4NO_2)_2]$ DFT (**3**).

| | | (1) | DFT (1) | (2) | DFT (2) | (3) | DFT (3) |
|---|---|---|---|---|---|---|---|
| | | | | Distances [Å] | | | |
| Ti-Ti | Ti1-Ti3 | 3.1690(11) | 3.1875 | 3.2016(16) | 3.1849 | 3.2060(12) | 3.1855 |
| | Ti1-Ti2 | 2.9427(12) | 2.9149 | 2.9488(16) | 2.9132 | 2.9521(13) | 2.9121 |
| | Ti1-Ti4 | 3.1446(12) | 3.1480 | 3.1456(15) | 3.1439 | 3.1508(12) | 3.1461 |
| | Ti2-Ti3 | 3.1566(11) | 3.1478 | 3.1532(17) | 3.1439 | 3.1617(13) | 3.1461 |
| | Ti2-Ti4 | 3.1738(13) | 3.1877 | 2.1859(17) | 3.1849 | 3.2009(12) | 3.1855 |
| | Ti3-Ti4 | 4.0386(16) | 4.0173 | 3.9255(16) | 4.0270 | 3.9510(13) | 4.0246 |
| Ti-($\mu_4$-O) | Ti1-O2 | 2.0457(30) | 2.0504 | 2.0599(39) | 2.0472 | 2.059(3) | 2.0466 |
| | Ti2-O2 | 2.0357(28) | 2.0504 | 2.0622(41) | 2.0472 | 2.052(3) | 2.0466 |
| | Ti3-O2 | 2.0820(27) | 2.0764 | 2.0603(38) | 2.0797 | 2.074(3) | 2.0796 |
| | Ti4-O2 | 2.0896(27) | 2.0767 | 2.0264(38) | 2.0797 | 2.042(3) | 2.0796 |
| Ti-($\mu_2$-O) | Ti1-O3 | 1.8326(37) | 1.8177 | 1.8643(40) | 1.8184 | 1.839(3) | 1.8178 |
| | Ti3-O3 | 1.8499(41) | 1.8178 | 1.8182(39) | 1.8184 | 1.826(3) | 1.8178 |
| Ti-($\mu_2$-OR) | Ti1-O11 | 1.9609(27) | 1.9600 | 1.9515(37) | 1.9581 | 1.944(3) | 1.9563 |
| | Ti1-O1 | 2.0042(28) | 2.0066 | 2.0133(38) | 2.0138 | 2.017(3) | 2.0147 |
| | Ti2-O21 | 1.9979(27) | 2.0067 | 2.0095(38) | 2.0138 | 2.020(3) | 2.0147 |
| | Ti2-O31 | 1.9633(28) | 1.9599 | 1.9858(38) | 1.9581 | 1.969(3) | 1.9564 |
| | Ti3-O1 | 1.9896(36) | 1.9988 | 2.0041(39) | 1.9938 | 1.993(3) | 1.9911 |
| | Ti3-O31 | 2.0981(29) | 2.0897 | 2.0698(45) | 2.0826 | 2.089(3) | 2.0850 |
| | Ti4-O11 | 2.0944(32) | 2.0897 | 2.1355(43) | 2.0826 | 2.114(3) | 2.0850 |
| | Ti4-O21 | 1.9985(30) | 1.9987 | 2.0182(44) | 1.9938 | 2.004(3) | 1.9911 |
| | | | | Angles [deg] | | | |
| Ti-($\mu_4$-O)-Ti | Ti3-O2-Ti2 | 100.10(12) | 99.41 | 99.80(17) | 99.25 | 100.05(12) | 99.36 |
| | Ti3-O2-Ti1 | 100.31(13) | 101.14 | 102.02(17) | 101.02 | 101.76(13) | 101.07 |
| | Ti2-O2-Ti1 | 92.28(12) | 90.60 | 91.36(17) | 90.72 | 91.79(12) | 90.704 |
| | Ti3-O2-Ti4 | 150.98(16) | 150.62 | 147.7(2) | 151.01 | 147.43(15) | 150.773 |
| | Ti2-O2-Ti4 | 100.58(13) | 101.14 | 102.34(18) | 101.02 | 102.83(14) | 101.07 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | Ti1-O2-Ti4 | 98.99(12) | 99.42 | 100.66(18) | 99.25 | 100.39(12) | 99.36 |
| Ti-(μ2-O)-Ti | Ti1-O3-Ti2 | 106.09(15) | 106.60 | 106.4(2) | 106.46 | 107.32(15) | 106.45 |
| Ti-(μ2-OR)-Ti | Ti1-O1-Ti3 | 105.04(15) | 105.46 | 105.72(18) | 105.26 | 106.16(14) | 105.35 |
| | Ti1-O11-Ti4 | 101.65(13) | 101.99 | 100.52(19) | 102.12 | 101.79(13) | 102.20 |
| | Ti2-O31-Ti3 | 101.97(14) | 101.98 | 102.04(18) | 102.12 | 102.35(13) | 102.19 |
| | Ti2-O21-Ti4 | 105.16(14) | 105.47 | 104.55(19) | 105.26 | 105.38(15) | 105.35 |

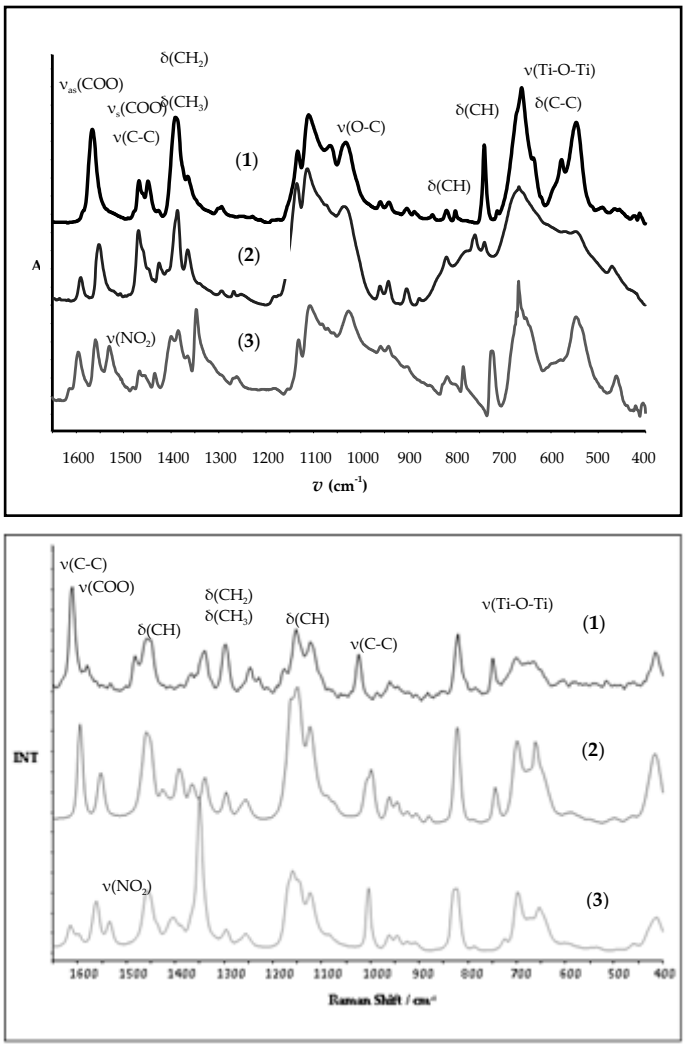


**Figure S1.** Infrared and Raman spectra of (**1**)–(**3**) complexes.

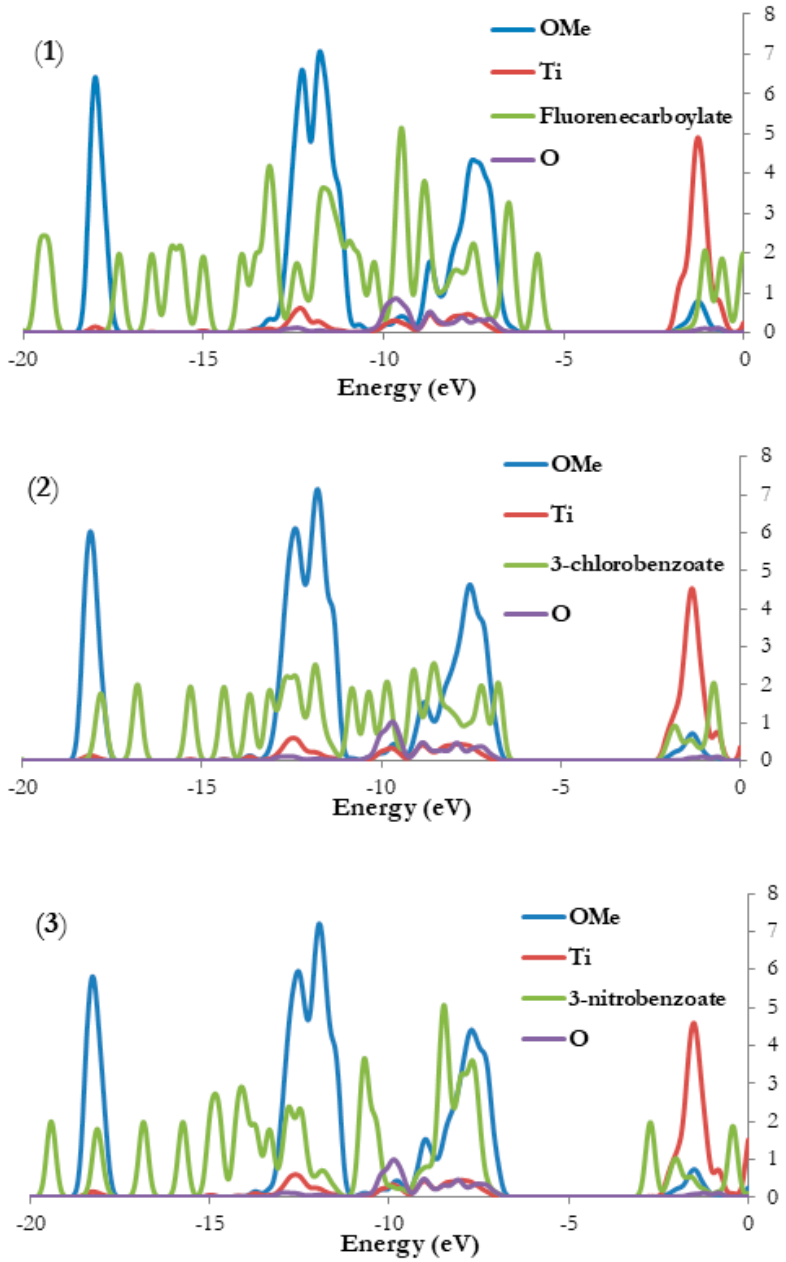


**Figure S2.** The calculated partial density of states of oxo-complexes (**1**), (**2**), and (**3**).

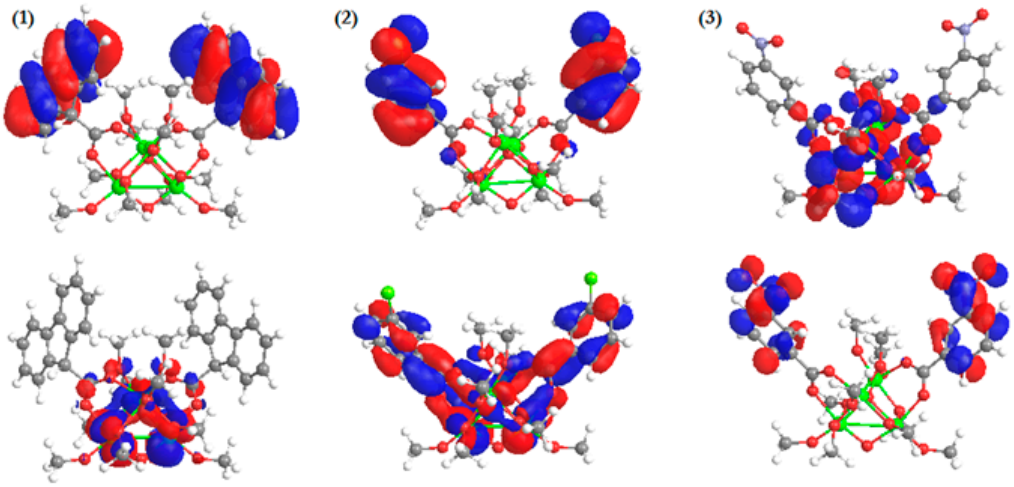


**Figure S3.** DFT calculated HOMO (top) and LUMO (bottom) molecular orbitals of (**1**), (**2**) and (**3**).