

Theoretical aspects of the reactivity of MN4 macrocyclics in electrochemical reactions

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We studied the electronic features of different adsorption and catalytic processes of some transition metal macrocyclic complexes (phthalocyanine) with Fe being the usual metal center. For oxygen molecule on iron phthalocyanine (FePc), both end-on and side-on configurations are found to be energetically favorable. However, the end-on adsorption configurations are more stable than side-on configurations. The activation barrier for the O-O bond cleavage for the side-on MN4-O₂ configuration is lower than that for the end-on MN4-O₂ configuration. On the other hand, we have built theoretical models based on DFT calculations from the formation of self-assembled monolayers (SAM) on a gold substrate and a thiolate ligand as an "anchoring" fragment of metallophthalocyanine, which leads to an interesting charge donation from the 4-aminothiophenol (4-ATP), 4-MP (4-mercaptopyridine) and 1-(4-mercaptophenyl)-2,6-diphenyl-4-(4-pyridyl)pyridinium tetrafluoroborate (MDPP) towards both gold substrate, Au(111) surface, and phthalocyanine, denoting an effective gold-MPc interaction mediated by the titled anchor ligands. The electrocatalytic studies carried out with Au/4-ATP/FePc and Au/MDPP/FePc electrodes show that the O₂ reduction takes place by the transfer of 4-electron to give water in contrast to a 2-electron transfer process observed for the bare gold. Theoretical calculations suggest the importance of the backbonding mechanism into the adduct formation, showing the relevance of the supporting gold surface on the electron-transfer process mediated by anchoring ligands. © Springer International Publishing Switzerland 2016.