# Organic-Transition Metal(TM) complex functionalized carbons for electrochemical applications: Geometries, electronic properties and

redox potentials

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## Introduction

In many electrochemical applications like catalysis, sensing and solar cells, ferrocene-based compounds play an important role as electron donor-receptors, which act as rapid and stable electron transfer mediators between the catalyst active centers and electrode. In other work, B-CNT coated electrodes have been found to have good sensitivity, selectivity, and stability for electrochemical sensing applications, better than glassy carbon or a pristine CNT electrode [1]. Thus, based on our previously-reported Cyclopentediene(Cp)TM/B-doped nanocarbon complexes[3], we reported a comprehensive study on the redox properties of CpTM/B-doped nanocarbons as a competitive replacement for the novel redox-active monolayer for electrochemical sensing and other applications, which may derive benefits from both the ferrocene and the B-doped nanocarbon. Other organic-TM/B-doped nanocarbons are also included in our study.

In this work, we use density functional theory (DFT) methods to calculate the redox potential and charge transfer mechanisms of CpFe/ B-doped, N-doped and pristine graphene complexes as well as porphyrinTM/ B-doped grahene in aqueous and acetonitrile solutions. The CpTM/B-doped nanocarbons are predicted to have competitive redox properties with ferrocene, revealing a promising way to create redox-active electrode materials for electrochemical applications.

### **Computational Methods**

In this work, we conducted a computational study using DFT on the structural, electronic and electrochemical properties of cyclopentene-transition metal (CpTM, with TM = Fe, Co, Ni) as well as porphyrin- transition metal (PORTM with TM = Fe, Zn, and Mn) complexes adsorbed on pristine, N-doped and B-doped graphenes. The solvation effects of water and acetonitrile were modeled by conductor-like polarizable continuum model (CPCM) solvation model. The redox potentials of those complexes were calculated from the DFT results following the protocol reported by Cossi et al.[2].

## **Results and Discussion**

The calculated redox potential vs. standard hydrogen electrode (SHE) of CpTM within different solvents (water and acetonitrile), sidechains on the Cp ring, and supports (pristine, B-doped, and N-doped) are shown in **Figure 1**. To find a suitable candidate of redox active material which has similar redox properties of ferrocene, the calculated redox potential vs. SHE of such material should be closed to the ferrocene's. As shown in **Figure 1**, only the CpFe complexes on B-doped supports show comparable redox potential with ferrocene in both water and acetonitrile, whereas the other metals or pristine and N-doped supports may not be used as ferrocene replacements. The small or negative potentials of Co, Ni complexes, N-doped and pristine complexes indicated that they are reduction agents. In addition, the trend of the sidechain effects on redox potential are generally consistent with the trends obtained with

isolated ferrocene molecules [2]. These results imply that the CpFe/B-doped nanocarbons are potential redox active electrode materials, competitive with ferrocene.



Figure 1. Redox potential of CpTM complexes with different TMs, sidechains and solvents.

#### Significance

The comparable redox potentials of CpFe/B-doped nanocarbons indicates a promising way to integrate redox active centers on high-performance B-doped nanocarbon electrodes. These redox active electrodes may have broad applications in electrochemical systems.

#### References

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