



# Metal (Co, Fe) tribenzotetraazachlorin–fullerene conjugates: Impact of direct $\pi$ -bonding on the redox behaviour and oxygen reduction reaction

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## ABSTRACT

Novel hexabutylsulphonyltribenzotetraazachlorin–fullerene (C<sub>60</sub>) complexes of iron (FeHBSTBTAC–C<sub>60</sub>) and cobalt (CoHBSTBTAC–C<sub>60</sub>) have been synthesized and their electrochemistry and oxygen reduction reaction (ORR) compared with their octabutylsulphonylphthalocyanine analogues (FeOBSPc and CoOBSPc). It is proved that electron-withdrawing substituents (–SO<sub>2</sub>Bu and C<sub>60</sub>) on phthalocyanine macrocycle exhibit distinct impact on the solution electrochemistry of these metallophthalocyanine (MPc) complexes. The more electron-withdrawing C<sub>60</sub> substituent suppressed ORR compared to the –SO<sub>2</sub>Bu in alkaline medium. FeOBSPc showed the best ORR activity involving a direct 4-electron mechanism, a rate constant of  $\sim 1 \times 10^8 \text{ cm}^2 \text{ mol}^{-1} \text{ s}^{-1}$  and a Tafel slope of  $-171 \text{ mV dec}^{-1}$ .

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## 1. Introduction

Over the years, first row transition metal (notably Fe and Co) phthalocyanine complexes have proved excellent electrocatalysts [1]. One of the means of tuning the redox properties of metallophthalocyanine (MPc) complexes is by introducing substituents on the peripheral positions of the phthalocyanine (Pc) rings. Butylsulfonyl (–SO<sub>2</sub>Bu) and fullerene (C<sub>60</sub>) are well known strong electron-withdrawing species whose impact, if introduced on the peripheral position of MPc complexes, has rarely been investigated. To our knowledge, there is no report on CoPc and FePc substituted with –SO<sub>2</sub>Bu or C<sub>60</sub>.

Despite the rich redox chemistry of the C<sub>60</sub> molecule [2], controversy still surrounds its application as an electrocatalyst. While some researchers [3,4] have reported the electrocatalytic properties of C<sub>60</sub> when immobilized on electrode surface, others believe that C<sub>60</sub> is electro-catalytically silent [5–7] and that such misleading claims of apparent “electrocatalytic” behaviour could be traced to a porous, partially blocked electrode, coupled with possible thin-layer effects [8,9]. Some researchers have anticipated that MPc–C<sub>60</sub> conjugates are likely to advantageously fine-tune the redox behaviour of Pc and MPc for the possibility of developing technologically

important devices. For example, Linssen et al. [10] reported the first covalently-bonded Pc–C<sub>60</sub> complex, while Torres group [11,12] reported the Pc–C<sub>60</sub> and subPc–C<sub>60</sub> adducts. Although these Pc–C<sub>60</sub> conjugates [10–12] exhibit remarkable redox properties due to the presence of the C<sub>60</sub>, the molecular orbitals of the Pc and C<sub>60</sub> appear to be independent of each other as the MOs of the Pc moiety were essentially unperturbed by the C<sub>60</sub> unit. To improve on this, Fukuda et al. [13] recently synthesized hexabutylsulphonyltribenzotetraazachlorin (HBSTBTAC, a phthalocyanine analogue) and nickel hexabutylsulphonyltribenzotetraazachlorin–C<sub>60</sub> (NiHBSTBTAC–C<sub>60</sub>), with the HBSTBTAC and C<sub>60</sub> moieties in close proximity thereby realizing strongly interacting  $\pi$ -electrons.

In this work, we report the synthesis, electrochemistry and oxygen reduction properties of FePc and CoPc species peripherally substituted with –SO<sub>2</sub>Bu or C<sub>60</sub> moieties. Cathodic reduction of oxygen is essential in the design and development of fuel cells. We show that these substituents have distinct impacts on the solution electrochemistry of the CoPc and FePc complexes as well as their oxygen reduction reaction (ORR) activity.

## 2. Experimental

### 2.1. Synthesis

1,2-Dicyanofullerene (1) [14] and 4,5-bis(butylsulfonyl)phthalonitrile (2) [15] were prepared according to the methods

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