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

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ABSTRACT

Novel hexabutylsulphonyltribenzotetraazachlorin–fullerene (C_{60}) complexes of iron (FeHBSTBTAC- C_{60}) and cobalt (CoHBSTBTAC- C_{60}) 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 ($-SO_2Bu$ and C_{60}) on phthalocyanine macrocycle exhibit distinct impact on the solution electrochemistry of these metallophthalocyanine (MPc) complexes. The more electron-withdrawing C_{60} substituent suppressed ORR compared to the $-SO_2Bu$ in alkaline medium. FeOBSPc showed the best ORR activity involving a direct 4-electron mechanism, a rate constant of $\sim 1 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and a Tafel slope of -171 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 ($-SO_2Bu$) and fullerene (C_{60}) 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 $-SO_2Bu$ or C_{60} .

Despite the rich redox chemistry of the C_{60} molecule [2], controversy still surrounds its application as an electrocatalyst. While some researchers [3,4] have reported the electrocatalytic properties of C_{60} when immobilized on electrode surface, others believe that C_{60} 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_{60} 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_{60} complex, while Torres group [11,12] reported the Pc- C_{60} and subPc- C_{60} adducts. Although these Pc- C_{60} conjugates [10–12] exhibit remarkable redox properties due to the presence of the C_{60} , the molecular orbitals of the Pc and C_{60} appear to be independent of each other as the MOs of the Pc moiety were essentially unperturbed by the C_{60} unit. To improve on this, Fukuda et al. [13] recently synthesized hexabutylsulphonyltribenzotetraazachlorin (HBSTBTAC, a phthalocyanine analogue) and nickel hexabutylsulphonyltribenzotetraazachlorin- C_{60} (NiHBSTBTAC- C_{60}), with the HBSTBTAC and C_{60} moieties in close proximity thereby realizing strongly interacting π -electrons.

In this work, we report the synthesis, electrochemistry and oxygen reduction properties of FePc and CoPc species peripherally substituted with $-SO_2Bu$ or C_{60} 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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described in the literature. Quinoline was distilled over CaH₂ under vacuum prior to use. The other reagents were used as supplied.

2.1.1. Preparation of 3a (FeHBSTBTAC-C₆₀)

A mixture of **1** (100 mg, 0.13 mmol), **2** (95 mg, 0.26 mmol) and (10 μL) of iron pentacarbonyl (Fe(CO)₅, Kanto) was suspended in chloronaphthalene (Nacalai) and heated at 190 °C for 2 h under argon. (CAUTION: Fe(CO)₅ is suspected to be a neurotoxicant and has been ranked as one of the most hazardous compounds to the ecosystem and human health; so it must be used with caution). After cooling to room temperature, the reaction mixture was poured into methanol and the resultant precipitate filtered off. The filtrate was vacuum-dried and the residue separated successfully, first by using short column of normal silica gel (CHCl₃) and finally with CHCl₃/MeOH (200:2 v/v) as eluent to obtain the first blue-colored fraction. Recrystallization from CHCl₃/methanol gave pure **3a** with 3.1% (16 mg). UV-vis (CHCl₃, λ_{max}/nm): 334, 612, 773. MASS (ESI-FTICR) (m/z): 1955.1919, Calcd for C₁₁₀H₆₀N₈S₆O₁₂FeNa: 1955.1897.

2.1.2. Preparation of 3b (CoHBSTBTAC-C₆₀)

The same procedure as reported for NiHBSTBTAC-C₆₀ conjugate [13] was adopted except that cobalt chloride was used as the metal salt. Briefly, a mixture of **1** (100 mg, 0.13 mmol), **2** (95 mg, 0.26 mmol), cobalt chloride dihydrate (23 mg, 0.14 mmol), and a catalytic amount of ammonium molybdate (120 mg) was suspended in distilled quinoline (1 mL) and heated at 190 °C for 2 h under argon. After cooling to room temperature, the reaction mixture was poured into methanol and the resultant precipitate filtered off. The filtrate was vacuum-dried and the residue separated successfully, first by using short column of normal silica gel (CHCl₃) and

finally with CHCl₃/MeOH (200:2 v/v) as eluent to obtain the first blue-colored fraction. Recrystallization from CHCl₃/methanol gave pure **3b** with 3.1% (16 mg). UV-vis (CHCl₃, λ_{max}/nm): 330, 612, 761. MASS (ESI-FTICR) (m/z): 1958.1898, Calcd for C₁₁₀H₆₀N₈S₆O₁₂-CoNa: 1958.1879.

2.1.3. Preparation of 4a (FeOBSPc)

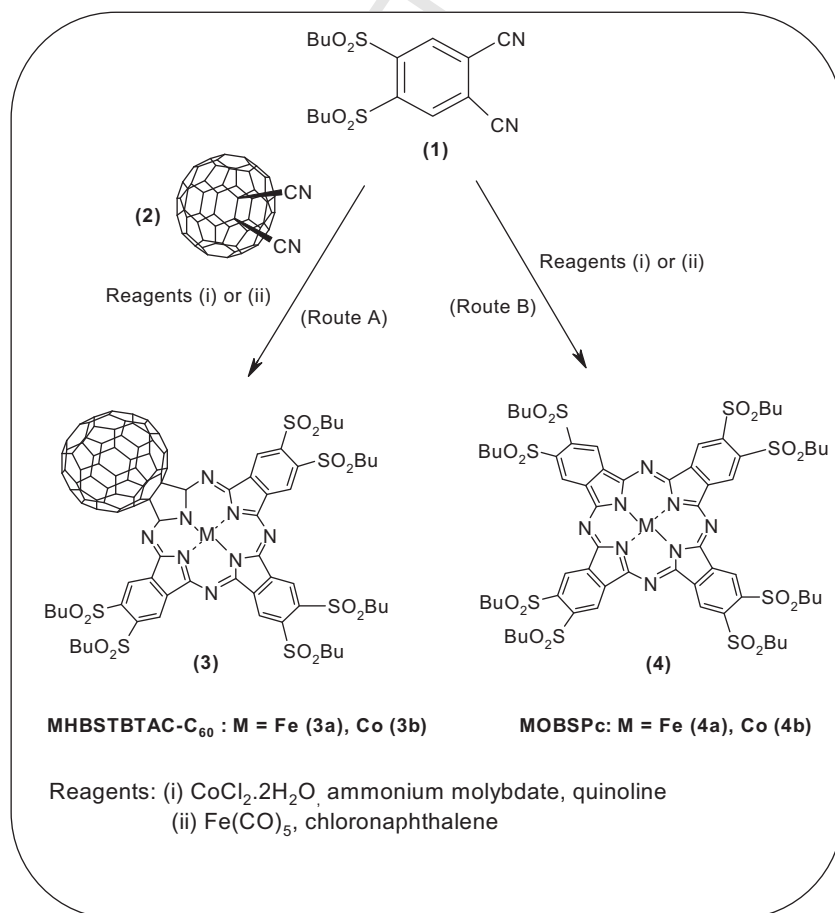
The same procedure, including amount of reagents, as for **3a** except that **2** was not used. UV-vis (CHCl₃, λ_{max}/nm): 360, 696 MASS (ESI-FTICR) (m/z): 1551.2714, Calcd for C₆₄H₈₀N₈S₈O₁₆FeNa: 1551.2700.

2.1.4. Preparation of 4b (CoOBSPc)

The same procedure as for **3b** except that **2** was not used. UV-vis (CHCl₃, λ_{max}/nm): 343, 678. MASS (ESI-FTICR) (m/z): 1554.2702, Calcd for C₆₄H₈₀N₈S₈O₁₆CoNa: 1554.2682.

2.2. Instruments and procedure

UV-vis spectra measurements were recorded using a Cary 300 UV-vis spectrophotometer, driven by Varian software version 3.0. All electrochemical studies were performed with Autolab PGSTAT 20, GPES 4.9 software (Eco-Chemie, Utrecht, The Netherlands). Solution electrochemistry was performed in ~1 mM of complex in dry DMF containing 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte under nitrogen atmosphere. Glassy carbon electrode (0.07 cm²), platinum rod and Ag|AgCl wire were used as the working, counter and reference electrodes, respectively.



Scheme 1. Synthetic routes for MOBSPc and MHBSTBTAC-C₆₀ (where M = Fe, Co).

Oxygen reduction reaction was performed with modified edge plane pyrolytic graphite electrode (EPPGE) fabricated in-house from EPPG plate (Le Carbone, Sussex, UK). Electrical contact with the disk was maintained through an inserted copper wire held in place with conducting silver varnish. A Ag|AgCl (3 M KCl) and platinum wire were used as reference and counter electrodes, respectively. The working electrode (0.30 cm²) for the rotating disk electrode experiment was fabricated in-house from an EPPG plate housed in an AUTOLAB-RDE Teflon cover. Prior to modification, the bare EPPGE was first polished with slurries of aluminium oxide nanopowder (Sigma-Aldrich), mirror finished on a Buehler felt pad and then subjected to ultrasonic vibration in acetone and ultrapure water respectively for 2 min. MOBSPc or MHBSTBTAC-C₆₀ species (2 mg) was dissolved in 2 ml DMF and ultrasonicated for 5 min. MOBSPc modified EPPGE (i.e., EPPGE-MOBSPc where M = Fe or Co) or EPPGE modified with MHBSTBTAC-C₆₀ (EPPGE-MHBSTBTAC-C₆₀ where M = Fe or Co) were prepared by dropping 15 μ L of a prepared solution on the EPPGE followed by drying in

a drying cabinet at 30 °C for 45 min. For the oxygen reduction experiments, 30 mL of 0.1 M NaOH solution was used as the electrolyte saturated with high purity nitrogen or oxygen. Ultra pure water of resistivity 18.2 M Ω cm was obtained from a Milli-Q water system (Millipore Corp., USA). All Other reagents were of analytical grade and were used as received from the suppliers without further purification.

3. Results and discussion

Scheme 1 summarizes the synthetic procedure employed. The ESI-FTICR and UV-vis data listed in the experimental section clearly confirm the synthesized products. Unlike the MOBSPc complexes that showed one B band (360 nm for FeOBSPc and 343 nm for CoOBSPc) and one Q band (696 nm for FeOBSPc and 678 nm for CoOBSPc), the MHBSTBTAC-C₆₀ complexes showed well-resolved split Q bands (612 and 773 nm for FeHBSTBTAC-C₆₀ and 612 and 761 nm for CoHBSTBTAC-C₆₀) of nearly equal intensities.

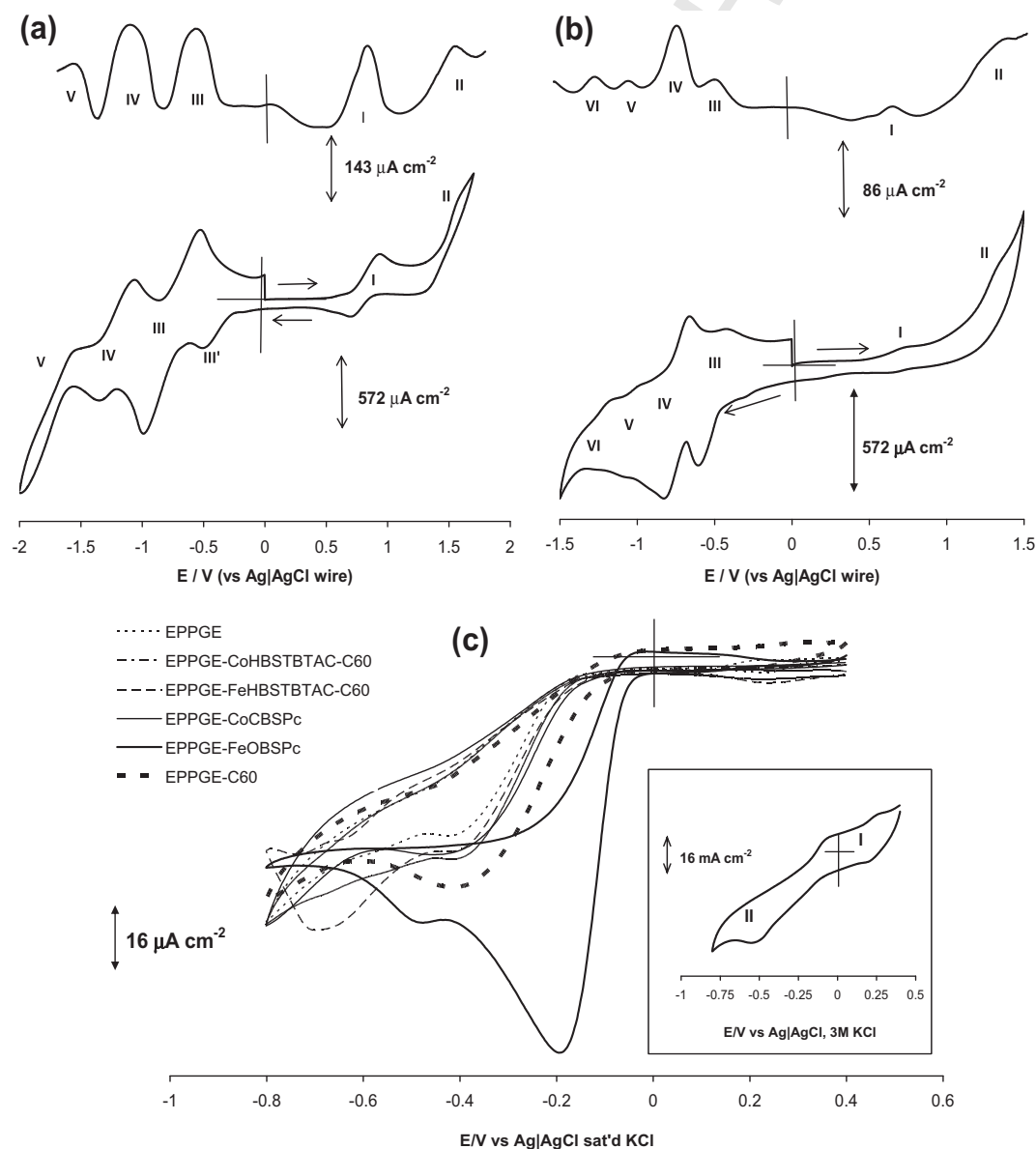


Fig. 1. Typical square wave voltammograms (upper) and cyclic voltammograms (lower) for FeOBSPc (a) and FeHBSTBTAC-C₆₀ (b) recorded in DMF containing 0.1 M TBAP. (c) Comparative cyclic voltammograms of the various electrodes in 0.1 M NaOH saturated with oxygen. Insert is CV of EPPGE-FeOBSPc in nitrogen-purged 0.1 M NaOH. Scan rate for the CV = 50 mV s⁻¹.

Table 1
Redox potentials of compounds recorded in DMF containing 0.1 M TBAP.

Compound	Potential, E_p or $E_{1/2}$ (V vs. Ag/AgCl wire)								
	6th red.	5th red.	4th red.	3rd red.	2nd red.	1st red.	1st ox.	2nd ox.	3rd ox.
C ₆₀				-1.42	-0.88	-0.30			
FeOBSPc				-1.62	-1.16	-0.67	0.76	1.48	
CoOBSPc				-1.61	-1.06	-0.58	0.32	1.63	
FeHBSBTAC-C ₆₀			-1.22	-1.02	-0.68	-0.45	0.66	1.31	
CoHBSBTAC-C ₆₀	-1.67	-1.39	-0.90	-0.62	-0.38	-0.05	0.48	0.53	1.54

The split Q bands recorded for the **MHBSBTAC-C₆₀** is in agreement with that observed for the **NiHBSBTAC-C₆₀** [13].

3.1. Solution electrochemistry

Fig. 1a and b shows typical cyclic voltammograms and corresponding square wave voltammograms obtained in DMF containing about 1 mM of FeOBSPc and **FeHBSBTAC-C₆₀** in 0.1 M TBAP (second scans). All the redox processes were diffusion-controlled as the plots of I_p vs. $u^{1/2}$ were linear. The values of the redox potentials are summarized in Table 1. From Table 1, we can conclude the following. First, the first reduction and oxidation processes of the MOBSPc and **MHBSBTAC-C₆₀** complexes are attributed to the metal centers ($M^{3+/2+}$ and $M^{2+/1+}$), respectively, in comparison with literature [16]. The other reduction processes of the MOBSPc complexes are ascribed to the Pc rings; while those of the **MHBSBTAC-C₆₀** complexes are due to Pc rings and the C₆₀ species. Peak III' seen at the MOBSPc species is ascribed to the electrolyte as it was unstable, disappeared at high scan rates or during repetitive scans. Second, the well-resolved second reduction peak of the **FeHBSBTAC-C₆₀** (peak IV) appeared as three reduction processes in the case of the **CoHBSBTAC-C₆₀** (IV–VI). Each of the three reduction processes is one-electron process each as the sum of their heights (voltammograms not shown) were comparable to the single sharp peak of the **FeHBSBTAC-C₆₀**. This suggests that the three processes for the **FeHBSBTAC-C₆₀** occur close to each other and thus overlap as one peak. Third, the reduction peaks of the **MHBSBTAC-C₆₀** are almost close to those of the C₆₀ alone, meaning that the involvement of the reduction processes of the C₆₀ in the assigned peaks of the M(II)/M(I) and Pc rings may not be completely ruled out; Future work is required to establish this possibility. Finally, it is interesting to observe that the reduction processes of the MOBSPc complexes occurred at more negative potentials compared to those of the **MHBSBTAC-C₆₀** complexes. Electron-withdrawing substituents are expected to reduce the electron density on the total conjugated MPc system leading to easier reduction (and more difficult oxidation), thus the lower potentials recorded for the **MHBSBTAC-C₆₀** complexes clearly suggest the higher electron-withdrawing influence of the C₆₀ on the MPc macrocycle compared to the **-SO₂Bu**.

3.2. Oxygen reduction reaction

Fig. 1c shows the comparative CV of the complexes studied in oxygen saturated 0.1 M NaOH. In highly alkaline solution the ORR goes to completion with only one peak observed due to four-electron reduction of oxygen to water [17]. Clearly, the **EPPGE-FeOBSPc** gave the best catalytic activity towards oxygen reduction, with less negative onset potential (**-0.02 V**) and current density of about twice higher than those of other electrodes. It is well known that symmetrically substituted **electron-withdrawing** substituents with inductive effects have the strongest influence in increasing MPc catalytic activity towards ORR if, and only if, they are incapable of forming direct **π -bond** with the macrocycle [18]. It

is to be noted that at C₆₀-modified gold electrode, Schiffrin's group [6] had attributed poor ORR activity to the size of the C₆₀ or the so-called "third body effect" of the adsorbed C₆₀ which are **electrocatalytically** silent. Thus, apart from the effect of direct **π -bonding** of the C₆₀ with the MPc, some possible contributions of the size of the C₆₀ may not be completely ruled out for our observed poor ORR activity of the **MHBSBTAC-C₆₀** conjugates.

From the CV of the **EPPGE-FeOBSPc** in the electrolyte (Fig. 1c inset), two weak couples, I (0.35 V) and II (**-0.5 V**), were observed, and if the processes involved are the same as those observed in the solution electrochemistry by other authors [19], these two couples could be attributed to $Fe^{3+/2+}$ and $Fe^{2+/1+}$, respectively. The two waves for oxygen reduction could be related to these two redox processes. It should be borne in mind that ORR with MPc complexes can proceed via the peroxide pathway where oxygen undergoes two-electron reductions to peroxide and then to water, or via a direct four-electron pathway involving a series of steps without the formation of detectable peroxide to give water. To corroborate this, rotating disk electrode (RDE) experiment was performed with the **EPPGE-FeOBSPc** (voltammograms not shown), and analysis of the data using the **Koutecky-Levich** theory [20] in the **range from -0.2 to -0.5 V**, gave approximately **4-electrons**, a rate constant of $\sim 1 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, a Tafel slope of **-171 mV dec⁻¹** with an α value of 0.35. These results suggest that both redox processes of the FeOBSPc ($Fe^{3+/2+}$ and $Fe^{2+/1+}$) mediate the reduction of oxygen to water in alkaline solution at a very fast rate. The low α value of 0.35 (rather than 0.5 usually observed for conductive electrodes) is attributed to electrode properties arising from such factors as non-uniformity of thickness and porosity, random mixture of pore diameters and lengths, thereby making some regions more conductive than others [21]. This is not surprising as our recent study [22] with electrochemical impedance spectroscopy proved that EPPGE exhibits constant phase elements, characteristic of electrode roughness, porosity and heterogeneities existing at the electrode/electrolyte interface.

4. Conclusion

Comparative electrochemistry and ORR of novel hexabutylsulphonyltribenzotetraazachlorin-fullerene (C₆₀) complexes of iron (**FeHBSHBSBTAC-C₆₀**) and cobalt (**CoHBSHBSBTAC-C₆₀**) have been compared with their octabutylsulphonylphthalocyanine analogues (FeOBSPc and CoOBSPc). We clearly prove that the substituents (**-SO₂Bu** and C₆₀) impact on the solution electrochemistry of these MPc complexes as well as their ORR activity. Importantly, the more electron-withdrawing C₆₀ substituent suppressed ORR compared to the **-SO₂Bu** in alkaline medium. FeOBSPc showed the best ORR activity compared to other electrodes investigated.

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