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Anion-dependent micelle formation using electro-generated ferrocene surfactants

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ABSTRACT

The syntheses and characterization of two ferrocene oils, 4-octyloxy-2-{5-[1,1,3,3-tetramethyl-3-(11-oxo-11-ferrocenyl-undecyl)-disiloxanyl]-pentyloxy}-benzoic acid 4′-undecyloxy-biphenyl-4-yl ester, **Fc1SiM** and an octakis(ferrocene) species, **Fc8Si8M**′ are reported, and their biphasic aqueous voltammetry contrasted. Surprisingly, both hydrophobic species undergo single-wave electrochemical dissolution. This can be advantageous to electroanalytical applications.

1. Introduction

Ferrocene is the archetypal electroactive mediator exploited for the detection of a wide variety of biologically-relevant and environmentally-important chemicals, via redox catalysis [1]. In this scheme, the main drawback is the decomposition of the 17-electron ferricinium species via reaction with dioxygen [2]. Nevertheless, given its general electrochemical reversibility, it is a versatile redox moiety and, in particular, is capable of being exploited to test novel-concept sensor designs. In this manuscript, we explore the biphasic electrochemistry of microdroplets [3,4] of two ferrocene-based redox oils (Fc_1SiM and Fc_8Si_8M' – see Scheme 1) immersed into aqueous electrolytes. Fc_1SiM contains a single ferrocene moiety; Fc_8Si_8M' is an octakis(ferrocene) species, and was selected since, if electron-exchange between the eight ferrocene species is fast on the voltammetric timescale [5–7], an eight-electron oxidation wave should be present. This is advantageous in electronanalytical chemistry as the Faradaic current (i_F) is proportional to the number of moles of electrons transferred heterogeneously (n): $i_F = nF \oint j\,dS$, so that the signal-to-noise ratio increases with n, under the caveat of fully supported electrolytes.

2. Experimental

2.1. Chemical reagents

All materials were purchased from the Sigma–Aldrich company in the purest commercially available form. Silica gel 60 (Merck) was used for column chromatography. TLC was performed on Silica gel plates (Merck, Silicagel F_{254}). Dichloromethane (DCM) was purchased from Fisher Scientific, UK as HPLC grade. All electrolytes were made using water taken from an Elgstat system, and with resistivity not less than 18 MΩ cm. All solutions were purged with impurity-free nitrogen (BOC Gases Ltd.) prior to experimentation. Thermal properties were investigated using a Mettler Toledo differential calorimeter (DSC 822^e) in nitrogen against an indium standard. Transition temperatures were determined as the onset of the maximum in the endotherm or exotherm.

2.2. 1-Ferrocenyl-undec-10-en-1-one (Fc1)

Undec-10-enoyl chloride was prepared by dissolving undec-10-enoic acid (1 eq), oxalyl chloride (1.2 eq) in DCM and 1 drop of DMF and stirred at room temperature until gas-evolution ceased, followed by solvent-removal under reduced pressure. To a stirred solution containing ferrocene (1.5 eq) and undec-10-enoyl chloride in dry DCM, cooled to about 5 °C, anhydrous $AlCl_3$ was added in small portions ($T < 10$ °C). The reaction mixture was maintained at room temperature, under stirring, for 7 h. The mixture was poured than on ice water and the organic layer was washed with NaOH (2%) and water, dried on $MgSO_4$ and concentrated. The crude compound was purified by column chromatography with DCM:hexane (5:1); red oil (67% yield). ^{1}H-NMR δ_H ($CDCl_3$): 5.8 (m, 1H, CH=), 5.0 (dddd, 2H, $=CH_2$); 4.75 (t, 2H, $=CH_2$), 4.45 (t, 2H, Fc), 4.16 (s, 5H, Fc), 2.68 (t, 2H, CH_2–CO), 2.03 (q, 2H, CH_2), 1.68 (cv, C–CH_2–C), 1.30 (m, 10H, aliphatic); ^{13}C-NMR δ_C ($CDCl_3$): 204.17, 138.83, 113.96, 78.94, 71.8, 69.6, 69.05, 68.1, 39.43, 33.5, 29.28, 29.25, 29.13, 28.86, 28.66, 24.32.

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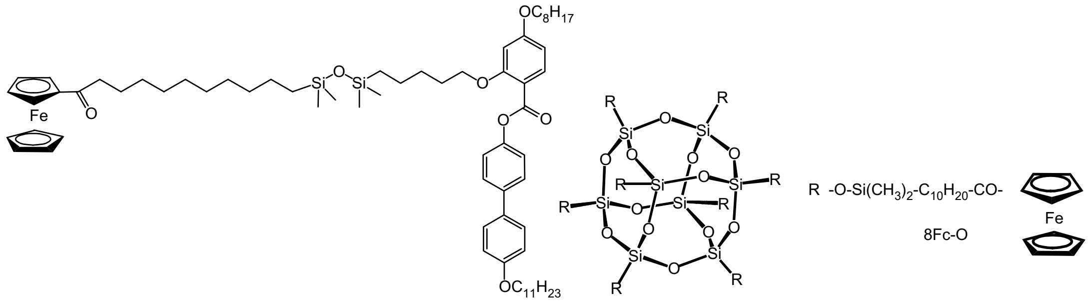

Scheme 1. Fc1SiM (left) and **Fc8Si8M′** (right).

2.3. 4-Octyloxy-2-[5-(1,1,3,3-tetramethyl-disiloxanyl)-pentyloxy]-benzoic acid 4′-undecyloxy-biphenyl-4-yl ester

The synthetic procedure for has been published in a previous work [8].

*2.3.1. **Fc1SiM***

To a stirred solution containing 1 eq of Fc1 of 4-octyloxy-2-[5-(1,1,3,3-tetramethyl-disiloxanyl)-pentyloxy]-benzoic acid 4′-undecyloxy-biphenyl-4-yl ester dissolved in dry toluene (15 ml) was added platinum(0)-1,1,3,3-tetramethyl-1,3-diviynldisiloxane (Karstedt catalyst) (10–20 drops) and dried compressed air bubbled through the reaction mixture for 1 min. The reaction was allowed to stir at room temperature over night. The solvent was then removed under reduced pressure and the residue purified by column chromatography with DCM:hexane (2:1) followed by size exclusion chromatography on sephadex column (LH20). Yield 51%; LC:N −9.5 °C Iso; ^{1}H-NMR $_{H}$ ($CDCl_3$): 8.3 (*d*, 1H, Ar), 7.51 (*dd*, 4H, Ar), 7.22 (*d*, 2H, Ar), 6.95 (*d*, 2H, Ar), 6.5 (*dd*, 2H, Ar), 4.76 (*t*, 2H, Fc), 4.46 (*t*, 2H, Fc), 4.17 (*s*, 5H, Fc), 3.99 (*m*, 6H, CH_2–O), 2.68 (*t*, 2H, CH_2–CO), 2.0–1.0 (*m*, 4H, aliphatic), 0.88 (*m*, 6H, aliphatic), 0.46 (*m*, 4H, CH_2–Si(C)), 0.0 (*s*, 12H, CH_3–Si); ^{13}C-NMR $_{C}$ ($CDCl_3$): 204,34; 164,02;

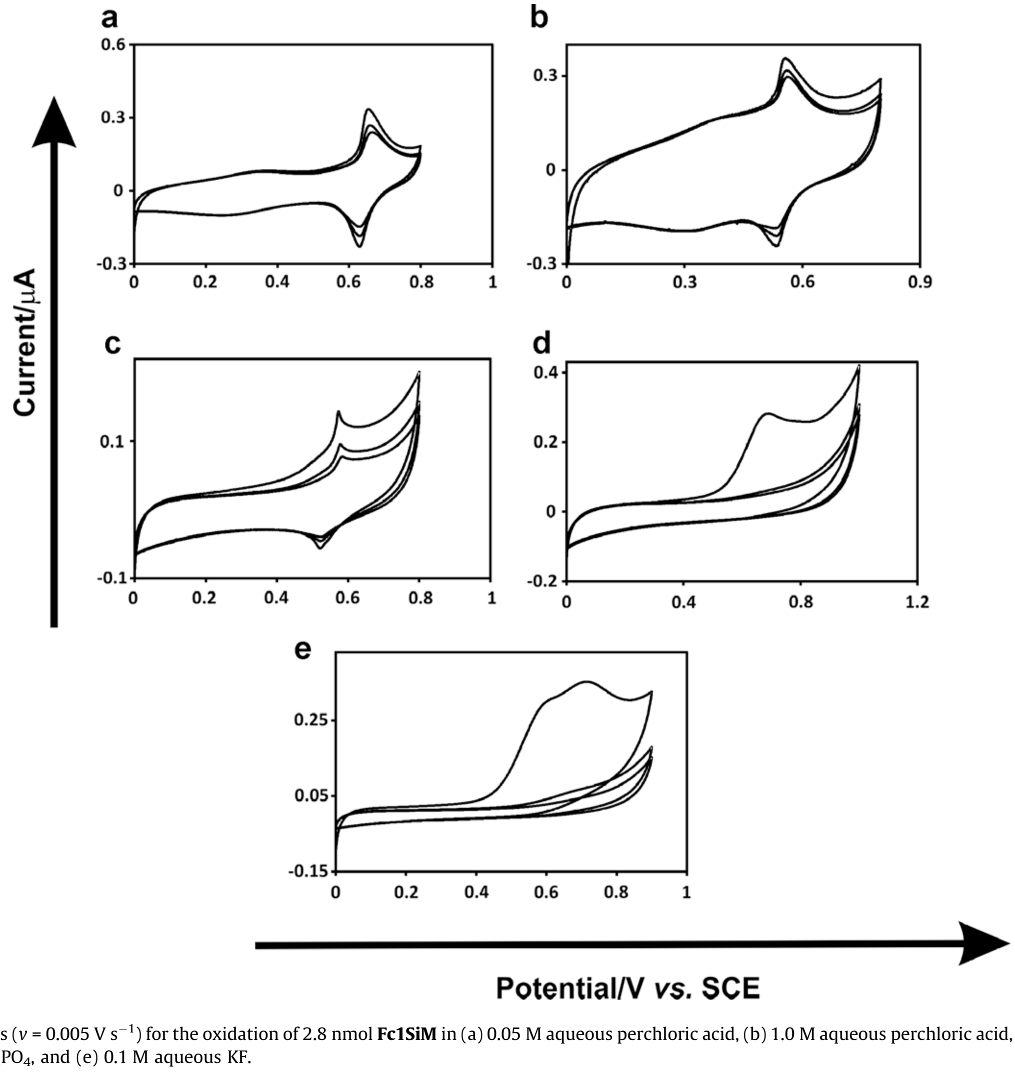

Fig. 1. Voltammograms (v = 0.005 V s^{-1}) for the oxidation of 2.8 nmol **Fc1SiM** in (a) 0.05 M aqueous perchloric acid, (b) 1.0 M aqueous perchloric acid, (c) 0.1 M aqueous KPF_6, (d) 0.1 M aqueous KH_2PO_4, and (e) 0.1 M aqueous KF.