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Short communication

High density heterogenisation of molecular electrocatalysts in a rigid intrinsically microporous polymer host

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ABSTRACT

A water-insoluble Polymer with Intrinsic Microporosity (or PIM, here for the particular case of the Tröger Base system PIM-EA-TB, BET area ca. 10^3 m^2 g^{-1}) is demonstrated to act as a rigid host environment for highly water-insoluble molecular catalysts, here tetraphenylporphyrinato-iron (FeTPP), surrounded by aqueous solution-filled micropores. A PIM-EA-TB film containing catalyst is deposited onto the electrode and immersed for voltammetry (i) with 4-(3-phenyl-propyl)-pyridine to give an organogel, or (ii) bare directly into aqueous solution. The porous host allows processes to be optimised as a function of solution phase, composition, and catalyst loading. Effective electron transfer as well as effective electrocatalysis is reported for aqueous oxygen and peroxide reduction. Given the use of completely water-insoluble catalyst systems, the methodology offers potential for application with a wide range of hitherto unexplored molecular electrocatalysts and catalyst combinations in aqueous media.

1. Introduction

High density heterogenisation of molecular catalysts and/or catalyst systems is desirable (i) to exploit the benefits of assembled molecular catalysts at electrode surfaces, (ii) to avoid catalyst losses due to dissolution and separation, (iii) to enable "families" or "ensembles" of catalysts and co-catalysts to be assembled into active films, and (iv) to allow screening of catalyst activity as a function of solvent system, electrolyte, ionic strength, or pH. Most commonly applied are direct surface immobilisation strategies based on adsorption of catalysts [1,2], electrostatic attachment [3], or covalent attachment via carbon [4] or ethynyl [5] bonds. These methods require suitable surfaces, high surface area, and carefully executed surface chemistry. An alternative strategy can be based on porous host materials such as conducting polymers [6], network polymers [7], zeolites [8], intercalation materials [9], and sol–gels [10], which in turn need to be immobilised or pasted [11] into the electrode material. In particular gels and polymer hosts are beneficial and readily applied, although stability of these host materials, ageing, cross-linking, and non-rigidity causing mobility of guest species can be problematic.

Recently, a novel family of highly rigid and therefore highly intrinsically microporous polymer (PIM) materials has been proposed [12,13]. In dry gas media these porous polymers allow gas separation [14] and gas storage [15]. When immersed in electrolyte media and in particular when carrying intrinsic charge (e.g. the poly-amine PIM-EA-TB when protonated, see Fig. 1A [16]), these rigid and microporous polymer materials become desirable for applications in electrochemistry [17,18].

In this report, it is demonstrated that the microporous PIM-EA-TB offers an ideal rigid (suppressing Ostwald ripening) environment for molecular catalysts, such as the water-insoluble model system FeTPP (see Fig. 1B). Fig. 1D represents a schematic depiction of the case of molecular FeTPP catalyst randomly distributed within the rigid host and surrounded by aqueous electrolyte. Fig. 1E depicts the case of a water-immiscible organic solvent, here 4-(3-phenyl-propyl)-pyridine or PPP [19], co-deposited into the porous PIM-EA-TB host to give an organogel, which is used here to characterise the chemically reversible one-electron transformation Fe(II/III)TPP (with coordination of PPP in L_1 and L_2 position, Fig. 1B) coupled to anion transfer from the aqueous phase. The aqueous system (Fig. 1D) is demonstrated for the electrocatalytic reduction of oxygen and of hydrogen peroxide.

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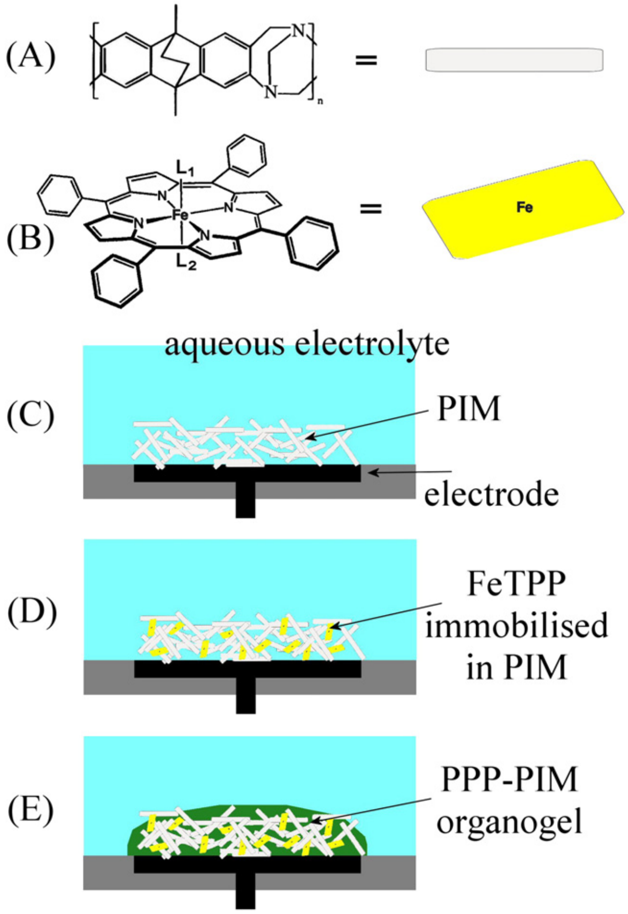

Fig. 1. (A) Molecular structure of PIM-EA-TB. (B) Molecular structure of FeTPP. Schematic drawings of (C) PIM immobilised onto an electrode, (D) with FeTPP immobilised into the rigid microporous structure, and (E) with PPP to form a separate organogel phase.

2. Experimental

2.1. Chemical reagents

4-(3-Phenylpropyl)-pyridine (97%), 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine iron(III) chloride (FeTPPCl), phosphoric acid (85 wt.%), sodium hydroxide (>97%), dimethylformamide (HPLC grade, >99.9%), $NaClO_4$, $NaPF_6$, $NaNO_3$, and hydrogen peroxide (35 wt.%) were obtained from Aldrich or Fisher Scientific. PIM-EA-TB was prepared following a literature recipe [16]. Solutions were prepared with filtered and deionized water of resistivity 18.2 MΩ cm from a Thermo Scientific water purification system.

2.2. Instrumentation

A potentiostat system (IVIUM Compactstat) was employed with a Pt wire counter electrode and a KCl-saturated calomel reference (SCE, Radiometer, Denmark). The working electrode was a glassy carbon electrode (3 mm diameter, BAS). The UV/Vis experiments were performed with a Varian UV–Visible spectrophotometer. All experiments were conducted at a temperature of 293 ± 2 K.

2.3. Procedures for electrode preparation

Solution A of PIM-EA-TB (1 mg cm^{-3}) in dimethylformamide (DMF) acidified with 5 μL $HClO_4$ was prepared. Solution B of FeTPPCl (1 mg cm^{-3}) in DMF solution was prepared. Then solutions A and B were mixed and 1 μL mixture deposited onto the glassy carbon electrode surface with solvent evaporation at 90 °C in an oven. A free-standing membrane 1:1 FeTPPCl:PIM was prepared by solution evaporation in a Teflon mould (see Fig. 2B). Films deposited onto glass slides were characterised by UV/Vis (Fig. 2A) and the characteristic Soret band at 414 nm [20] is observed.

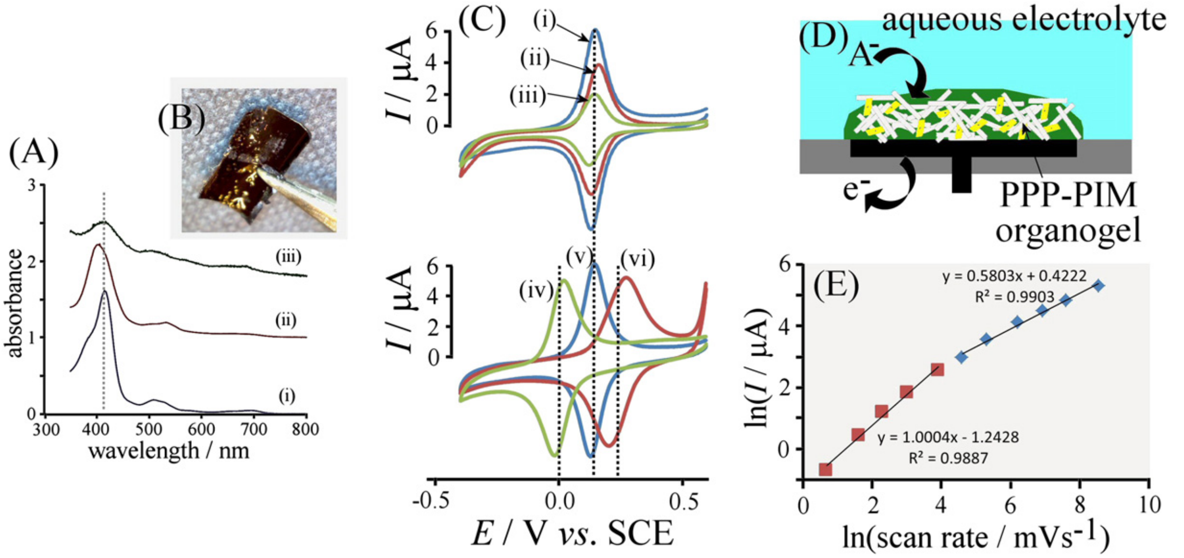

Fig. 2. (A) UV/Vis spectra for (i) 0.1 mg cm^{-3} FeTPPCl in DMF, (ii) a film of 1:5 FeTPPCl:PIM, and (iii) a film of 5:1 FeTPPCl:PIM (ii and iii are offset for clarity). (B) Photograph of a free-standing PIM-FeTPP membrane. (C) Cyclic voltammograms (scan rate 20 mV s^{-1}) for the oxidation of FeTPP immobilised into PIM and coated with PPP (to give an organogel phase separate from the aqueous phase) immersed in 0.1 M phosphate buffer pH 7 with 0.1 M $NaClO_4$ for FeTPP:PIM weight ratios (i) 1:1, (ii) 1:5, and (iii) 1:20. Also shown are data for 1:1 FeTPP:PIM immersed in phosphate buffer with (iv) 0.1 M $NaPF_6$, (v) 0.1 M $NaClO_4$, and (vi) $NaNO_3$. (D) Schematic drawing of the liquid|liquid anion transfer process coupled to the $FeTPP^{+/0}$ redox process at the electrode surface. (E) Plot (double logarithmic) of the peak current for the oxidation of FeTPP:PIM 1:1 in phosphate buffer with 0.1 M $NaClO_4$ as a function of scan rate.