

## Supplementary Information

### General procedures

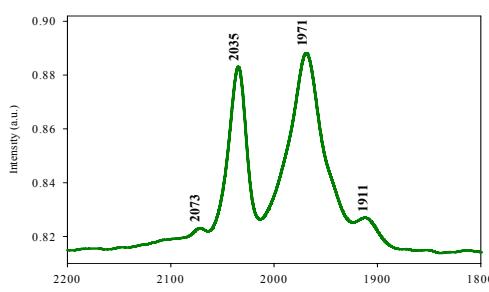
All manipulations were carried out under an inert atmosphere using vacuum line or Schlenk techniques. Solvents were degassed and dried prior to use.

Electrochemical measurements were made using a three electrode, three compartment cell fitted with a platinum counter electrode and either a Ag wire pseudo-reference electrode or SCE. The working electrode was a Pt disc of geometric area  $0.28\text{ cm}^2$ . Cyclic voltammetry and other measurements were made using an Autolab PGSTAT 30 with GPES version 4.9 software.

Procedures for the synthesis of the pyrrole monomer A, its electrochemical polymerisation and the cleavage of the cystine bonds are as in reference 4. The thickness of the polymer films were determined directly by integration of the current time response for the oxidation of the polymer backbone (Pickett *et al* Dalton Trans 1993, 3695) or indirectly from the charge passed during oxidative growth of the film (Passos *et al* J Electroanal Chem 1997 **435** 189). Procedures for loading with the cubane cluster are given in reference 4.

### Modification of the polymer confined cluster

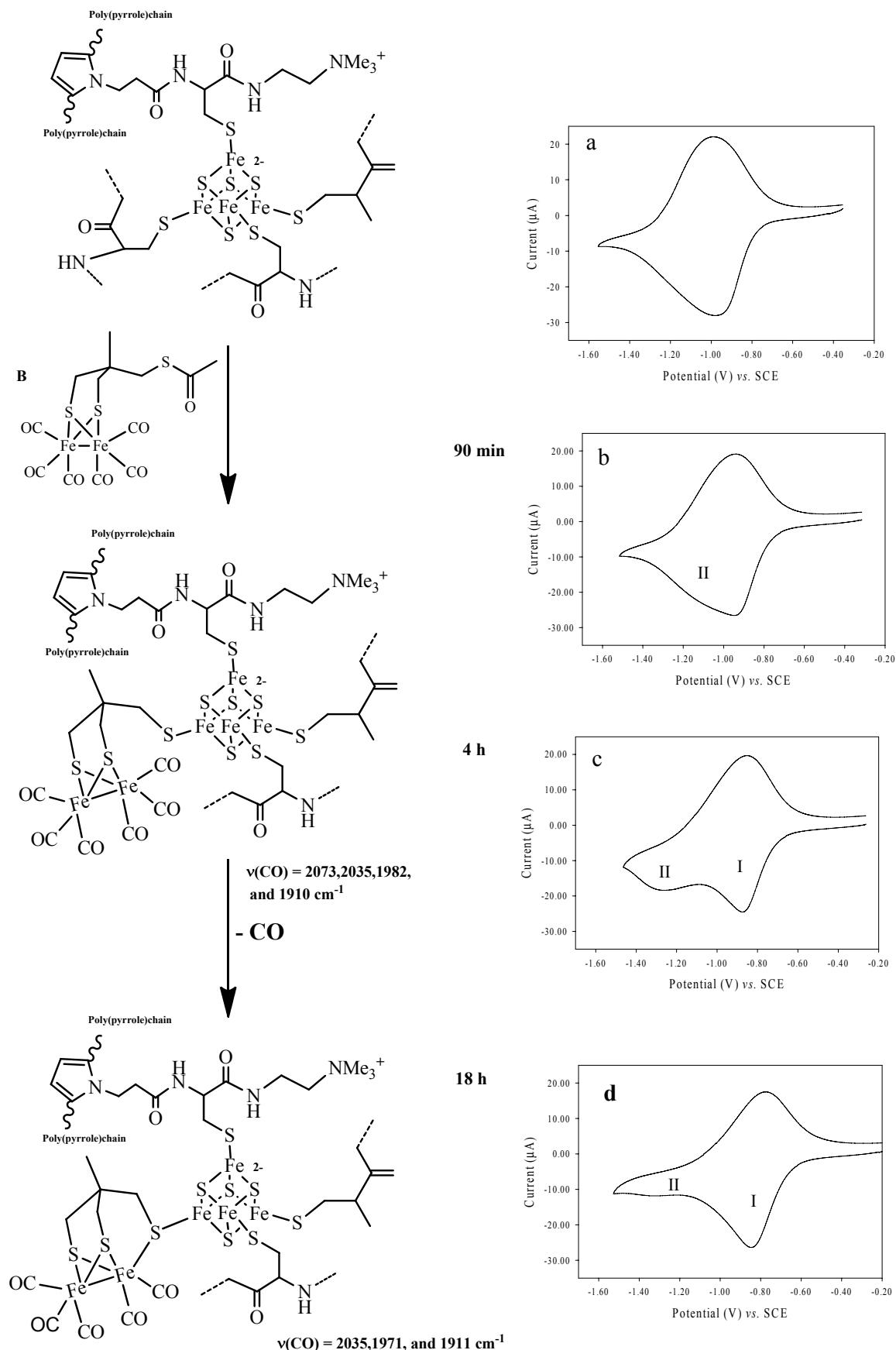
Films containing the confined cluster were modified by exposure to a 3mM solution of **B** in 0.2M  $[\text{NBu}_4][\text{BF}_4]$ -MeCN in an inert atmosphere box running at  $< 2\text{ppm O}_2$  under nitrogen. The films were removed from the reagent, washed copiously with MeCN and dried under a stream of nitrogen before being examined by reflectance FTIR on a Bruker Vertex 80 spectrometer. The infra-red response after exposure to **B** for 18h at RT is shown below in Figure 1. The bands correspond closely to those reported for a synthetic H-Cluster assembled in a parallel fashion in solution.<sup>5</sup>



**Figure 1** FTIR spectroscopy on a wasnea ana area jum ayer exposing a polymer confined cluster to the di-iron thioacetyl subsite **B**, 18h.

At 18 hours the cyclic voltammetric response of the modified film was also measured in fresh 0.2M  $[\text{NBu}_4][\text{BF}_4]$ -MeCN. The charge associated with the reversible one electron reduction was measured by integration of the current-time for the cyclic voltammetric responses before and after modification using the Autolab GPES software and this showed the conversion took place with a yield of more than 80%.

Intermediate stages of conversion are shown by Scheme 3. The detection of process II, shifted negatively from the parent peak, is attributed to an intermediate formed before CO loss and thiolate bridge formation. The  $E^{0/}$ -potential is thus close to that for a simple 'alkylthiolate' subsite and the observation of an infrared stretch near  $2073\text{ cm}^{-1}$  (remote from overlapping CO bands, supports this).



**Scheme 3** Assembly of an artificial H-cluster framework in an electropolymer film on a platinum disk.  
Electrode area  $0.28 \text{ cm}^2$ . Scan rate of voltammogram  $20 \text{ mV s}^{-1}$  in MeCN  $0.2\text{M} [\text{NBu}_4][\text{BF}_4]$ .