Electronic Supplementary Material (ESI) for Dalton Transactions.
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Electronic Supplementary Information (ESI) for

An Fe(III)-doped coordination polymer of Mn_{13}-clusters with improved activity for the oxygen reduction reaction

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Part I: Experimental Section

1. Structural determination

All powder X-ray diffraction (PXRD) analyses were performed on a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å) using a step size of 0.05°. Fourier transform infrared (FT-IR) spectra were taken on a Nicolet Magna 750 FT−IR spectrometer in the 4000−500 cm^{-1} region by using KBr pellets.

2. Electrochemical characterization

ORR measurements were carried out in a three-electrode glass cell. The data were recorded using a CHI760 D. The synthesized samples were used as the working electrode for electrochemical characterizations. The current density was normalized to the geometrical surface area and the measured potentials *vs.* Ag/AgCl were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation. A flow of O_2 was maintained over 0.1M KOH electrolyte during electrochemical measurements. The working electrodes were scanned for several times before the data for polarization curves were collected.

3. Synthesis of Mn_{13}-polymer

Typically, a mixture of $MnCl_2.4H_2O$ (0.197g), $KMnO_4$ (0.033g), tert-butylphosphonate acid (0.140g), 4,4'-trimethylenedipyridine (0.303 g) and CH_3OH (40 ml) was stirred for 5 h, and then the solution was filtered. The CH_3OH evaporated at room temperature, and the Mn_{13}-polymer samples were formed after two weeks.

4. Synthesis of Fe@Mn_{13}-polymer

The fresh Mn_{13}-polymer was successively washed with H_2O before immersing it in $FeCl_3$ (20 mM) solution for one 24 hours. Further, the obtained Fe@Mn_{13}-polymer was washed with water three times before use.

5. Fe@Mn_{13}-polymer coated on glassy carbon electrode

The as-synthesized Fe@Mn_{13}-polymer was ultrasonically dispersed in the mixture of 1.5 ml of Nafion solution (0.05 wt.% water solution), and then transferred onto the glassy carbon electrode with a loading amount of ~ 0.23 mg cm^{-2}. The resulting electrode was subjected to overnight solvent evaporation in air.

6. Mn_{13}-polymer coated on glassy carbon electrode

The procedure for preparation of Mn_{13}-polymer coated on glassy carbon electrode was the

same as that for Fe@Mn_{13}-polymer except for using Mn_{13}-polymer instead of Fe@Mn_{13}-polymer.

7. Pt/C coated on glassy carbon electrode

The procedure for preparation of **Pt/C** coated glassy carbon electrode was similar to that for **5**.

Part II: Supplementary Results

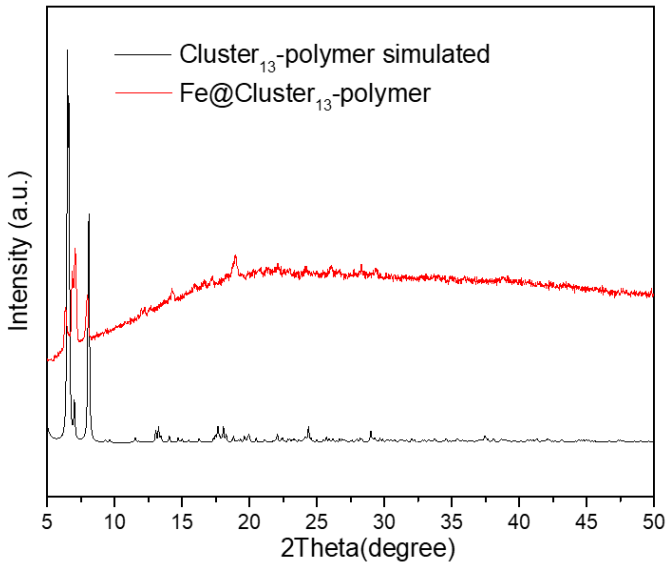

Figure S1. The PXRD pattern of Fe@Mn_{13}-polymer compared with the simulated pattern of original Mn_{13}-polymer.

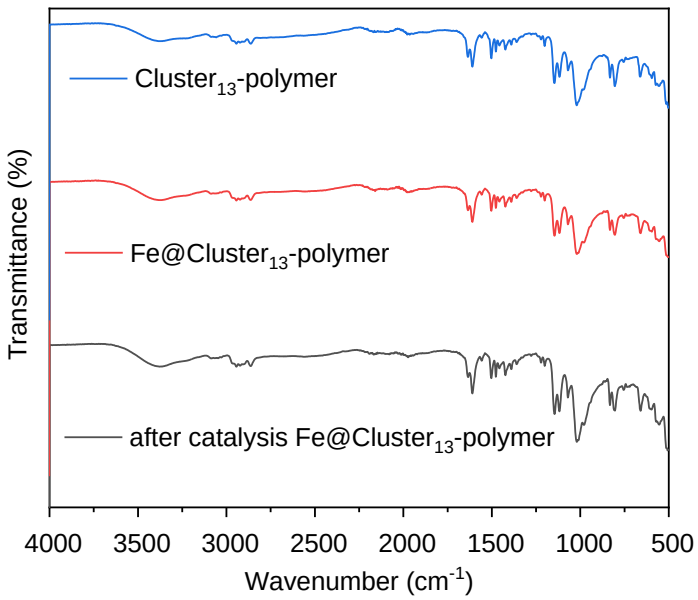

Figure S2. FTIR spectra of Mn_{13}-polymer and Fe@Mn_{13}-polymer (before and after ORR test).

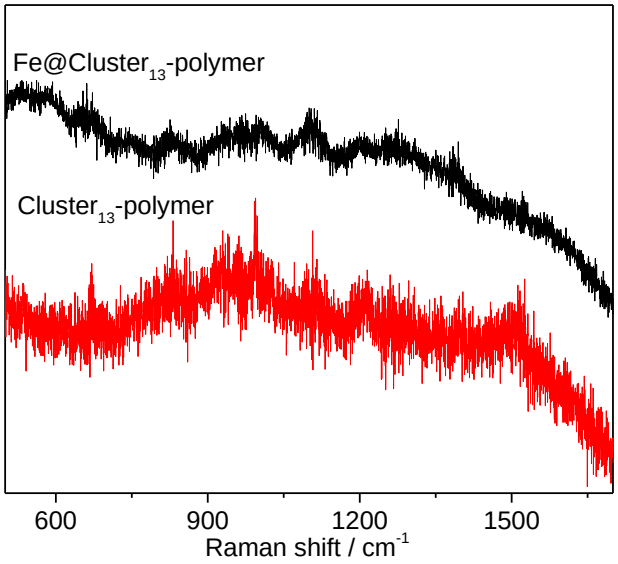

Figure S3. Raman spectra of Mn_{13}-polymer and Fe@Mn_{13}-polymer.

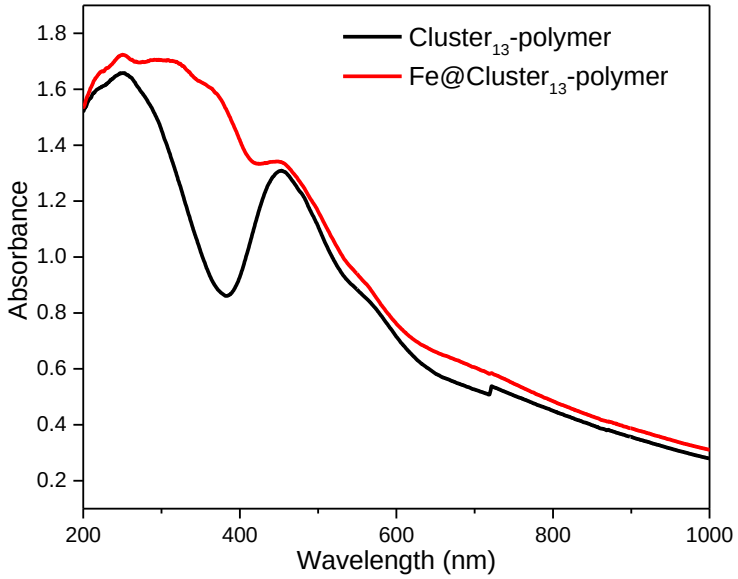

Figure S4. UV−vis spectra of as-prepared Mn_{13}-polymer and Fe@Mn_{13}-polymer.

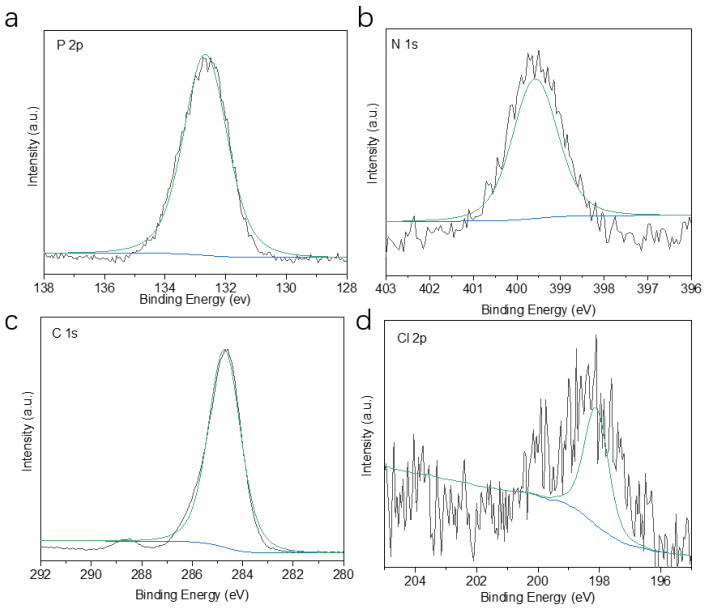

Figure S5. High resolution XPS spectrum of Fe@Mn13-polymer in the (a) P 2p (b) N 1s (c) C 1s (d) Cl 2p regions.

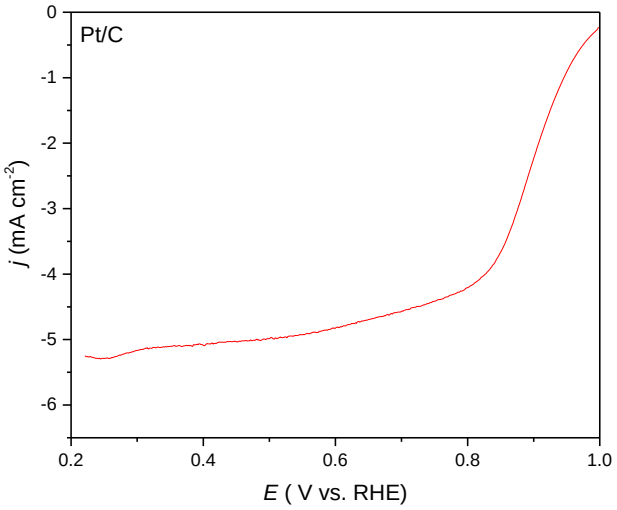

Figure S6. LSV of Pt/C in an O_2-saturated 0.1 M aq KOH solution.

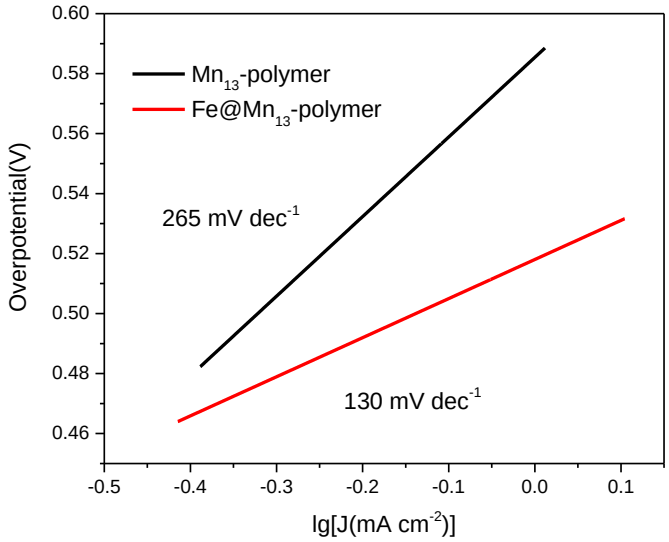

Figure S7. Tafel plots of Mn_{13}-polymer and Fe@Mn_{13}-polymer in 0.1M KOH aqueous solution.

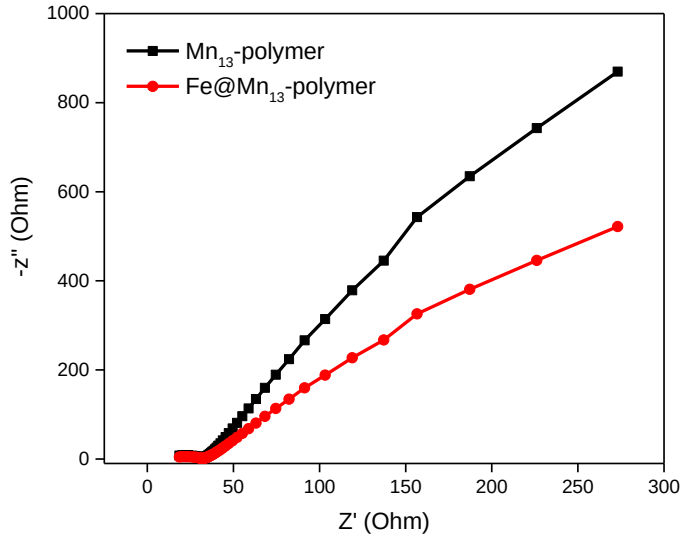

Figure S8. EIS of Mn_{13}-polymer and Fe@Mn_{13}-polymer electrocatalysts under ORR.

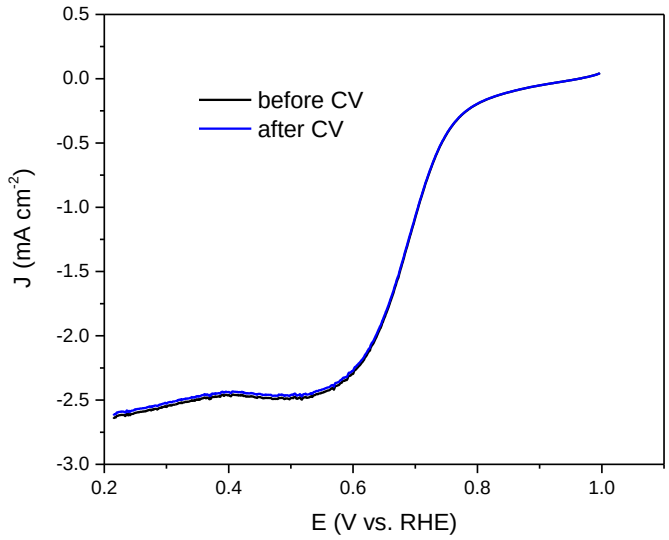

Figure S9. LSV of Fe@Mn_{13}-polymer in an O_2-saturated 0.1 M aq KOH solution after 5000 continuous cycles.