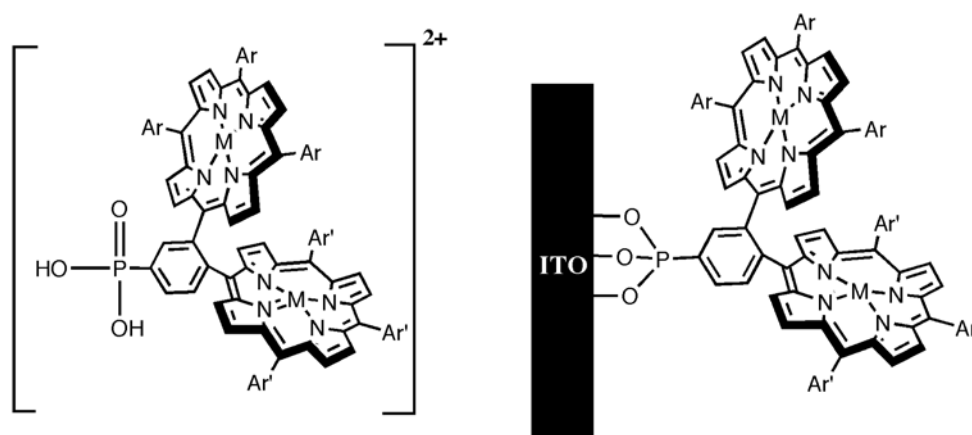


Efficient water oxidation with manganese and cobalt porphyrin dimers assembled on metal oxide surfaces

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To secure our increased demand of energy, a clean and renewable source should replace the current unclean and temporary fossil fuels. Nature provided us an efficient way of converting the abundant solar energy into chemical energy using water in a process known as photosynthesis. So far, a limited success was achieved in mimicking photosynthesis artificially, mainly due to the lack of suitable catalysts that can efficiently oxidize water to oxygen at a low overpotential. In the present study we fabricated manganese and cobalt porphyrin dimers with a phosphonate tether to fix strongly on the surface of metal oxide electrodes and use the assembly as efficient heterogeneous catalysts for water oxidation to oxygen.

The fabricated manganese and cobalt porphyrin dimer catalysts bearing a phosphonic acid tether, M₂(porD)-PO(OH)₂ (Fig. 1) (M = Mn^{III} or Co^{III}) were synthesized by a stepwise method and purified by a flash column chromatography. They were characterized by traditional spectroscopic techniques.



1a. M = Mn^{III}, Ar, Ar' = -C₆F₅ **2a.** M = Co^{III}, Ar, Ar' = -C₆F₅
1b. M = Mn^{III}, Ar, Ar' = -C₆H₂(CH₃)₃ **2b.** M = Co^{III}, Ar, Ar' = -C₆H₂(CH₃)₃
1c. M = Mn^{III}, Ar = -C₆F₅, Ar' = -C₆H₂(CH₃)₃ **2c.** M = Co^{III}, Ar = -C₆F₅, Ar' = -C₆H₂(CH₃)₃

Fig 1. Structure of manganese and cobalt porphyrin dimers bearing phosphonate tether and schematic representation of their attaching to ITO electrode.

Soaking a pre-cleaned ITO electrode in an 1 mM ethanolic solution of the catalysts resulted in a stable phosphonate surface binding of them on the ITO surface as indicated from the UV-vis absorption spectra measurements.

The cyclic voltammetric behavior of **catalyst**|ITO assemblies was investigated in Na₂B₄O₇ (25 mM)/NaClO₄ (0.1 M) aqueous solution at different pHs. While manganese-containing catalysts exhibit catalytic discharge current for water oxidation in acidic, neutral, and basic solutions at low overpotentials, the cobalt containing ones show water oxidation in neutral and basic conditions only. Efficient water oxidation was achieved from all the assemblies at low overpotentials.