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Metallophthalocyanine based redox active metal-organic conjugated microporous polymers for OER catalysis

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We report the design and synthesis of two Co^{2+} and Zn^{2+} phthalocyanine (PC) based redox active metal-organic conjugated microporous polymers (MO-CMP), CoCMP and ZnCMP respectively, obtained by Schiff base condensation reaction. CoCMP, where Co^{2+} is stabilized by N4-coordination of PC, has shown stable and effcient electrocatalytic activity towards OER with a low overpotential of 340 mV.

Conjugated microporous polymer (CMP) materials are derived from π -conjugated aromatic building block. Owing to the porosity, these materials have been extensively used for energy storage, catalysis, sensing etc.¹ Recently. CMP materials decorated with metal ions have attracted significant attention due to the metal driven applications of the resulting metal-organic conjugated microporous polymers (MO-CMP).² Phthalocyanines (PCs) are nitrogen rich redox active conjugated macrocycle, possessing N4-coordination site for metal ion.³ The planar and rigid N4-coordination provides high stability to the metal ion and makes them easily accessible for various metal based applications.⁴ Metallophthalocyanines have therefore been used extensively for energy harvesting and catalysis.⁵ Han and co-workers have reported Co²⁻ phthalocyanine based CMPs as an efficient photosensitizer for the singlet oxygen generation.^{2a} PCs are also well known electron donors^{5a} and with integration of electron acceptors, redox active donor-acceptor systems can be realized. On the other hand, oligo-(p-phenyleneethynylenes) (OPEs) are a class of π -conjugated linear organic chromophores which possess phenyl rings connected through rigid alkyne bonds.⁶ Notably, the linear and highly conjugated backbones of OPEs are advantageous for the facile charge transport.' Our group has reported that a suitable alkyl chain substitution on the OPE backbone alters the physical state, ranging from liquid crystallinity, gels to dispersible materials.⁸ The side chains of OPE backbone also plays a crucial role in regulating the nanoscale morphology of the resulting material.

Considering the individual advantages of the metallophthalocyanine macrocycle and OPE linker, we have



Scheme 1. Synthesis of metal-organic conjugated microporous polymer (MO-CMP); CoCMP and ZnCMP.

designed and synthesized two new redox active MO-CMP materials (CoCMP and ZnCMP) by integrating them to develop electrocatalysts for water oxidation, which is an important half cell reaction for the energy devices like metal-air batteries and regenerative fuel cells.⁹ However, the sluggish reaction kinetics of the oxygen evolution reaction (OER) due to the involvement of four electrons in the reaction mechanism is the main obstacle in the water oxidation.¹⁰ Therefore, design and synthesis of an OER electrocatalyst with low over potential and fast reaction kinetics with high stability is of paramount importance.¹¹ Transition metal ions, particularly redox active Co²⁺ ion based materials have drawn immense interest for designing OER catalysts due to its multiple stable redox states.¹² These materials were mainly prepared by Co doping in the porous organic polymer or by pyrolizing organicinorganic hybrid material.^{13, 11a} However, metal doping strategy is associated with the drawbacks of leaching as well as difficulties in the quantitative control of the metal ion that eventually affects both activity and stability of the catalyst. Recently, Das and co-workers have reported "ship in a bottle strategy" for designing a metal organic framework (MOF) based OER catalyst.^{5b} Here, the mononuclear Co²⁺ complex was locked in the confined space inside the MOF and acts as a catalytic centre.

In this communication, we report the design, synthesis and characterization of two new MO-CMP based OER catalysts. The amount of Co^{2+} in CoCMP and Zn^{2+} in ZnCMP was quantified by ICP, EDX, and XPS, and found to be 1.7 and 1.5%, respectively. Both the polymers showed stable charge separated state at

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Fig. 1. Characterization of MO-CMP compounds; (A) PXRD and (B) CO₂ adsorption data at 195K of CoCMP and ZnCMP, (C) FESEM and (D) TEM image of CoCMP (E) EDX analysis of CoCMP.

room temperature as realized by EPR spectroscopy. This was further supported by density functional theory (DFT) calculation. Notably, the intrinsically encapsulated Co^{2+} ion in the organic framework was found to be the catalytic centre for the OER. In the electrochemical OER study of CoCMP, an anodic peak started at 1.57 V that accounts for an overpotential of 340 mV. The role of permanent porous rigid framework was examined and found to be essential in preventing the metallophthalocyanine aggregation and consequently increase the catalytic performance and stability.^{2a} The Zn²⁺ containing MO-CMP was found to be inactive towards OER catalysis. This clearly explained the importance of Co^{2+} ion for the OER catalysis.

Both the MO-CMPs (CoCMP and ZnCMP) were synthesized by schiff base condensation reaction^{2a} between metallophthalocyanine tetraamine and a newly synthesized 4,4'-(2,5-bis(pentyloxy)-1,4-phenylene)bis(ethyne-2,1-diyl)

dibenzaldehyde (OPE-5)) (Scheme 1 and Figure S1-S2). Obtained MO-CMPs were characterized by elemental analysis, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), infrared (IR) and ¹³C-NMR.¹⁴ Porous nature of the materials was confirmed by the CO₂ adsorption experiment. The similar FTIR spectra of both the compounds were expected due to the similar functionality (Figure S3). A very intense peak at 1610 cm⁻¹ was found in both the compounds. This is apparently characteristic of the formation of polymer via imine bond (-C=N) formation. Importantly, a peak in the fingerprint region at 830 ($vM^{2+}=N$) ensured the presence of metal ion in the PC ring.^{2a} A peak at 2206 cm⁻¹ is attributed to the alkyne bond (-C \equiv C-) of the OPE-5 unit. The solid state ¹³C NMR was performed for ZnCMP (Figure S4). The most important imine carbon (-C=N-) peak is found at 156.0 ppm which confirms the polymer formation. The alkyl (- CH_n) and alkoxy (- OCH_2) carbons peaks were found at 18.6 and 60.1 ppm, respectively, which confirm the presence side chain of the OPE-5. The carbon of the heterocycle ring of PC appears deshielded at 167.8 ppm. The PXRD was performed within the range of 2θ value 2-35 (Figure 1A). The broad peak at $2\theta = 26.7^{\circ}$ (d = 3.30 Å) in CoCMP and

 26.2° (d = 3.40 Å) in ZnCMP corresponds to the interlayer separation and indicate the presence of strong π ... π stacking in both the compounds. A peak at low angle region of 2θ = 4.6 (d = 19.19 Å) in CoCMP and 4.9 (d = 18.02 Å) in ZnCMP correspond to the distance between two metal centre of the PC units bridged by the OPE linkers and also indicates the semi crystalline nature of both the polymers. Thermogravimetric analysis suggests high thermal stability for both the compounds (Figure S5). After initial weight loss which corresponds to the solvent molecules, both MO-CMPs show thermal stability up to 300 °C without any significant weight loss. Surface morphology of CoCMP was studied using FESEM and TEM by making dispersion of the polymer in ethanol. FESEM analysis showed the formation of semi spherical morphology which aggregates to form fractal like structures (Figure 1C). Energy dispersive X-ray (EDX) measurement indicated the presence of 1.7% cobalt (II) in the polymer (Figure 1E). High resolution TEM analysis showed layered morphology (Figure 1D) which was also found in low resolution TEM as well (Figure S6). XPS analysis of CoCMP further confirmed the presence of Co, C, N, and O elements in the framework (Figure 2A and S7). The XPS spectrum of Co can be deconvoluted into two components. The Co 2p XPS peaks at 773.8 and 800.2 eV can be assigned to $2p_{3/2}$ and $2p_{1/2}$, respectively (Figure 2A).^{15, 11b} Three different peaks of C1s spectrum at 278.0, 285.6 and 286.7 eV indicate the presence of three different types of carbon and can be attributed to C-C, C-N/C-O and C=C/C=N, respectively. The peak at 532.1 eV in the O 1s spectrum confirms the presence of the alkoxy side chain (C-O-C) of the OPE-5. XPS survey spectra of N 1s shows three bands; 386.8 eV for imine C=N, 401.6 eV for nitrogen which connects two pyrrole rings in the PC and 409.5 eV for metal coordinated pyrrole nitrogen. The amount of metal ions was further quantified by ICP experiment. ICP-AES data revealed the presence 1.7% of Co^{2+} and 1.5% of Zn^{2+} ion in CoCMP and ZnCMP, respectively.

To analyse the porous nature of these polymers, we carried out the adsorption study (Figure 1B). Both the polymers were activated at 140 °C under vacuum for 8 h before performing the gas adsorption measurement. Both the MO-CMPs showed type II adsorption profile for N_2 at 77 K (Figure S8). However, type I adsorption profile for CO_2 at 195 K (1 atm pressure)



Fig. 2. (A) XPS peak correspond to Co(II) in CoCMP, (B) EPR spectrum of CoCMP in solid state (C) DFT calculations show HOMO on cobalt phthalocyanine (bottom) and LUMO on the OPE backbone (top) of CoCMP.

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Fig. 3. Related OER activity for CoCMP, ZnCMP and CoPC: A) CV, B) LSV and C) corresponding Tafel plot of CoCMP D) 1000 cycles of LSV of CoCMP in 0.1 M KOH at scan rate of 50 mV/s and rotation speed of 1600 rpm, E) LSV comparing CoCMP, ZnCMP and Co-PC, F)100 cycles of LSV of Co-PC.

demonstrated the micro-porosity in both the compounds. Both MO-CMPs showed around 25-28 cc/g CO₂ uptake and the Langmuir surface area of the CoCMP and ZnCMP were found to be 106.47 and 101.34 m²/g, respectively. The non-inclusion of N₂ and poor CO₂ uptake can be attributed to the long alkyl chain of the OPE-5 occupied pore surface.

Electron paramagnetic resonance (EPR) study was performed with both the MO-CMPs in the solid state. In the CoCMP, a broad signal at g = 2.25 is attributed to the low spin Co(II) complex (Figure 2B). A sharp and intense signal at g = 4.37 is a triplet marker, indicating the presence of two cobalt PC units in close proximity.¹⁶ This intimates the presence of π ... π stacking in the polymer in an eclipsed fashion. Notably, a sharp peak at g = 1.99 in CoCMP and g = 2.00 in ZnCMP (Figure S9), represent the redox active nature of polymers and indicates the formation of stable charge separated species.¹⁷ Further, to get more insight about the charge separated behavior, we have performed density functional theory (DFT) computations for both CoCMP and ZnCMP. The electron donation property of metallophthalocyanine is well documented, however, we wanted to explore the acceptance property of the conjugated OPE backbone. In CoCMP, the highest occupied molecular orbital (HOMO) was situated on the Co-PC units. The energy difference between the HOMO and lowest unoccupied molecular orbital (LUMO) on the OPE backbone was found to be 2.17 eV (Figure 2C). This suggested that PC is the donor and OPE is the acceptor in this donor-acceptor stable charge separated system. In ZnCMP, the similar electronic distributions were found with the energy difference of 2.19 eV (Figure S10A). The energy difference indicated semiconducting nature of the highly conjugated polymer that could be effective in electrocatalytic activity. Furthermore, the DFT calculation of the water (H_2O) and hydroxide ion (OH) indicated that the electron transfer occurs from HOMO of OH⁻ to the LUMO of MO-CMPs (Figure S10B).

Electrocatalytic performance of both the MO-CMPs towards OER was studied by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) in a three-electrode cell configuration in 0.1 M KOH. The CV of CoCMP, at a scan rate of 50 mV/s and rotation speed of 1600 rpm (Figure 3A) showed onset of water oxidation at a potential of 1.57 V. The LSV (Figure 3B) at the same scan rate and rotation speed also showed an onset at 1.57 V with a lower overpotential of 340 mV which is comparable^{5b} to the present state-of-art electrocatalysts. A maximum current of 13 mA/cm² was obtained at a potential of 1.84 V. The linear region in the corresponding Tafel slope (Figure 3C) showed a slope of 87 mV/decade. The low Tafel slope and the lower overpotential, explains the fast and the facile kinetics of the oxidation process. Stability and cyclability of the CoCMP were examined by chronoamperometry (CA) and LSV, respectively. The chronoamperometric curve recorded at an applied potential of 1.75 V for 12 h (Figure S12), showed an initial increase in the current density followed by a gradual decrease with 91% retention of current density. The initial increase of current density was probably due to the activation of the surface of the electrocatalyst. During the OER, an insulating layer of oxygen bubbles were observed on the electrode surface, which obstructs the diffusion of charges and consequently decreases the current density.^{13a} As prompted by the 1000 cycles of LSV (Figure 3D), there was an infinitesimal increase in the activity of CoCMP after 1000 cycles which again might be due to the activation of the catalyst surface. Roughness factor (RF) gave an estimate of the electrochemically active surface area (ECSA) which in turn was reflected in the activity of the catalyst. To interpret the infinitesimal increase in the activity, we calculated RF of the catalyst before 1st cycle and after the 1000th cycle and it was found to be 154 and 157, respectively (Figure S11) which explains the possible activation of the catalyst surface and consequently justifies the increase in the current density. Another parameter that testifies the performance of a catalyst is its turnover frequency (TOF).¹⁸ TOF of CoCMP was calculated following the reported procedure,^{19, 18} both after the first cycle and the 1000th cycle of LSV and was found to be 0.29 s⁻¹ and 0.20 s⁻¹, respectively.

To attest the role of metal ion in the catalysis, we performed the water oxidation using Zn²⁺ containing ZnCMP as well. LSV of ZnCMP (Figure 3E) showed no catalytic activity towards OER. Hence it can be inferred that presence of Co²⁺ dictates the decent electrocatalysis shown by CoCMP. The next question in our mind was the necessity of the framework. To answer this, we studied the OER with the discrete Cophthalocyanine (Co-PC) unit as the electrocatalyst. The LSV of Co-PC (Figure 3F) at same experimental conditions showed a diminished current density at 1.85 V. The onset was at 1.70 V with overpotential of 470 mV. The declined catalytic activity of Co-PC could presumably be due to aggregation of the Co-PC units^{2a} which may restrict an effective accessibility of the active sites. A rigid and conjugated framework provides periodicity to the catalytic site along with the facile electron transportation. This eventually minimizes the probability of aggregation of the catalytic centre. Also, the permanent porosity in the framework helped the diffusion of substrate to the catalytic sites. The stability of the Co-PC monomer was studied by running 100 cycles of LSV. Figure 3f showed the deteriorated activity of Co-PC at 100th cycle which was due to leaching of cobalt species noticeable under naked eye (Figure S13). Leaching of cobalt decreases the number of active sites and hence explains the reduced activity. To ascertain no leaching of cobalt from CoCMP into the electrolytic solution, ICP was recorded both before and after 1000 cycles of LSV. CoCMP showed no appearance of Co in the electrolytic solution after 1000 cycles. Therefore, CoCMP exhibited no leaching of cobalt sites from the framework. This further proved the necessity of framework.

In summary, we have designed new N4 coordinated Co²⁺ containing phthalocyanine based porous conjugated organic polymer which has potential for catalysing OER. Interestingly, we observed that the enmeshed mononuclear Co(II) with even low loading (1.7 %) in rigid organic framework shows efficient electro-catalytic activity. CV and LSV showed an anodic current onset at 1.57 V with overpotential of 340 mV and Tafel slope of 87 mV/decade. The consistent catalytic performance of the CoCMP even after 1000 cycles endorses its excellent stability without leaching of the metal ions. On the other hand the diminished stability and the leaching of CoPC into the solution explained the necessity of a framework. The inactivity of ZnCMP towards OER exhibits the importance of the judicious selection of metal ion while designing the catalyst.

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Conflicts of interest

There are no conflicts to declare.

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