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Electrocatalytic activity and chemical sensor application of Mn-MOF: synthesis, crystal structure and photo luminescent properties

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Abstract

A solvothermal method was used to synthesize a Manganese metal-organic framework (Mn-MOF), [Mn(Tpa)(Mi)(DMF)] (Tpa = Terephthalic acid, Mi = Methylimidazole, DMF = Dimethylformamide). The Mn-MOF molecule has a three dimensional network in which the θ ranges from 5.942−50 with monoclinic I2/a space group. The final full matrix least-squares refinement over F² is converged on R₁ = 0.0558, wR₂ = 0.1696 through GOF = 1.095. Mn-MOF shows a strong luminescence along with red-shift, which indicates that these are the potential candidates for various luminescent applications. Electro catalytic activities of Mn-MOF electrode have also been tested for in 5 mM K₄FeCN₆ and K₃FeCN₆ in 0.5 M KCl solution. The electrochemical sensor detection of ascorbic acid (AA) in Mn-MOF was used as a buffer solution (pH-7.0). The ascorbic acid peak potential is a great deal nearer to the Mn-MOF electrode peak potential is ΔEp = 0.062 V. These results indicate that Mn-MOF electrode exhibits a very good electro catalytic activity and good chemical sensor by a quick reply in favor of ascorbic acid detection.

1. Introduction

Metal-organic frameworks (MOFs) are more important porous solids based on the complexity of molecular complexes. As MOFs display interesting topological descriptions and visual structures [1], the construction and planning of new MOFs has been studied as one of the major topics in coordination chemistry. MOFs are generally built through the coordination of metal clusters and organic linkers through extensive potential applications such as chemical/bio-sensor, heterogeneous catalysis [2] molecular magnetism [3] photoluminescent property [4] and gas storage [5]. Hydrothermal, solvothermal, microwave, etc techniques can synthesize the MOFs. These methods normally involve high temperatures and pressures [6]. To obtain novel MOFs, the modification of secondary building units (SBUs) and the layout of preferred organic linkers are committed to a large extent. The well-known materials have been commonly used as octahedral, triangular-shaped SBUs and paddle wheel to create exciting structures in specific solvent systems [7]. Using high-yield synthesis, MOFs can prevail, and low-temperature economical methods under solvothermal systems are typical techniques, but microwave, ultrasonic, electrochemical and diffusional overtures have been studied. Due to the development of tunable structures, solvothermal synthesis has recently gained a lot of interest [8]. Although this method synthesized a large number of MOFs, the same templating agents are generated by static inorganic ions or organic molecules to produce equivalent MOFs [9]. The architecture of MOFs is generally built on the basis of metal clusters and organic linkers being organized. The latter are coordinated with the so-called’ secondary building units’ in which metal clusters are vertices of the built frameworks. However, numerous factors that need to be taken into account when resembling the synthesis of new metal-organic frameworks, apart from the statistical principle, are temperature, concentration, pH, and solvent polarity. Annually, unusual global climate change due to greenhouse effects and the decline in fossil fuel demand improved energy utilization and management, particularly electrical energy. One of the promising ways to overcome these problems is to harness and store electrical energy for future use [10, 11]. Supercapacitor has recently emerged as a key enabling electrical
energy storage technology that provides a low-cost alternative energy source to replace rechargeable batteries for different applications [12]. A significant increase in a supercapacitor’s storage capacity can be achieved through the development of new nano-structured materials with high surface area capable of large numbers of load/discharge cycles leading to much longer operating lives. Metal-organic frameworks (MOFs) are undoubtedly the most versatile porous material with a high surface area as MOFs offer a wide range of structures that can be adjusted to a wide variety of metal ions with a number of organic connectors [13]. While significant progress has been made in the synthesis of the variety of MOFs, the application of MOFs has been relatively less successful. Although MOFs have been demonstrated for use in catalysis and gas storage materials, no reports on the application of MOFs in an electrical energy storage device have been reported to date. The relatively low chemical stability of MOFs is the major problem for electrocatalysis, as these reactions are performed in electrolyte solutions (mostly water-based) and usually require high acidity/basicity. Compared to MOF derived materials such as carbon, metal, metal oxide, and their composites, MOFs and MOF-based composites were therefore much less studied. Nevertheless, most MOFs have been produced with high chemical stability in water and even under highly acidic/alkaline conditions, some of which have been used successfully as electrocatalysts [14, 15]. Electrochemical capacitors, also known as SCs, have gained more popularity because they pledge to use material as an energy resource due to their high energy and power density, long service life, quick charge/discharge cycle, and environmentally friendly Overall, SC charging storage mechanisms can be classified into two types: Faradaic pseudo capacitors and electrical double-layer capacitors (EDLCs) [16]. Ascorbic acid is a well-known high-value vitamin in many physiological, biomedical and pathological research reactions [17, 18]. Ascorbic acid (AA) is a well-known vitamin of extreme importance in various physiological, biomedical and pathological studies [19, 20]. AA is an electrically active multi-modified electrode, but its oxidation means low selectivity and high overvoltage [23, 24]. AA was intended to examine the Mn-MOF-CPE capacity performance as a sensor with such a demanding bio molecule purpose. It is a personalized electrode that is electrically active, but its oxidation includes high uninvited overvoltage and compact selectivity [25, 29]. To achieve competent electrodes for recognition of ascorbic acid, the potential for oxidation must be lowered and the selectivity must be increased. MOFs have gained considerable recognition because of their charming structures, primarily MOFs have been evaluated as one of the leading candidates for sensing materials due to their distinctive characteristics of crystalline structured structures, high biocompatibility, tunable pore sizes, etc [30].

2. Experimental

2.1. Materials and methods

All the chemicals such as Manganese nitrate hexahydrate, Terephthalic acid, N, N-dimethylformamide (DMF) etc, used in this research work were of analytical grade, obtained from SDFCL (sd fine chem. Limited). Methylimidazole and chloroform were obtained from Spectrochem Pvt. Ltd. All of these were reagent grade chemicals and used as they received. The reactors used were stainless steel autoclaves with Teflon liners of 60 ml capacity. The Matri (Kerala) hot air oven was used for heating the autoclaves. SV Scientific Sonicator was used for uniform dispersion of the reaction solution. All the electrochemical characterization and measurement experiments were carried out in CHI 608E electrochemical analyzer with the three-electrode system.

2.2. Synthesis of Mn-MOF

A mixture of Mn(NO$_3$)$_2$·6H$_2$O (1.0 gm), Terephthalic acid (0.70 gm), were dissolved separately in 15 ml of DMF with mild stirring and then added about 0.5 ml of 1-methylimidazole to get a clear solution. The resulting solutions were transferred to a autoclave and heated in a oven at 120 °C for 72 h. Then the reaction system allowed to cool to room temperature. Obtained shiny white coloured crystalline material was filtered and

Figure 1. Scheme of the formation of Mn-MOF.
repeatedly washed with fresh DMF several times followed by chloroform. Finally, the product was dried at room temperature for 24 h. The scheme of the formation of Mn-MOF is as shown in the Figure 1.

2.3. Characterization techniques

The above product was characterized by studying the vibrational properties of the functional groups on Shimadzu 8400 S FTIR spectrophotometer using KBr pellets within the range of 400–4000 cm$^{-1}$. Powder x-ray diffraction study has been carried out using BrukerD8 Advance x-ray powder diffractometer with CuKa radiation, at $\lambda = 0.1541874$ nm to obtain the information on the nature of the product (crystalline or amorphous), phase structure and purity. FE-SEM images were taken on the Zeiss field emission scanning electron microscope. The crystal information data were collected at 293 K Using Olex2 instrument. The structure was solved with the ShelXT structure solution program using ShelXL refinement package with CGLS minimisation. All the electrochemical characterization and measurement experiments were performed with CHI 608E electrochemical analyzer with three-electrode system consisting of a bare carbon paste electrode (BCPE) as working electrode, platinum wire as auxiliary or counter electrode and saturated calomel electrode (SCE) as a reference electrode.

3. Results and discussion

3.1. Structural description

A single crystal data of Mn-MOF [Mn(Tpa)(Mi)(Dmf)] was collected on a Nova diffractometer. The crystal was set aside at 293 K during data collection. Using Olex2, the structure was solved through ShelXT. The structure resolution program use refining and Intrinsic Phase by the ShelXL refinement package using CGLS minimisation. Mn-MOF three dimensional (3D) frameworks based on SBUs. The range of $\theta$ was from 5.942–50. The structure was solved in monoclinic I2/a space group. The entire non-hydrogen atoms were distinguished anisotropically, the Mn-MOF contains both two Terephthalic acid and 1-methylimidazole groups in the asymmetric unit. The issue must exist well-known such former following description data are steady through the crystal structure. The final full matrix least-squares refinement over $F^2$ converged to $R_1 = 0.0558$, $wR_2 = 0.1696$ through GOF $= 1.095$.

3.1.1. Bond lengths and bond angles of Mn-MOF:

The Mn1-O bond lengths range from 1.261(5) to 2.400(3)Å can be regarded as normal for this type of coordination environment. The strong distortion of the trigonal prism, reflected by angles varying from 44.6 (6) to 169.08° (16)° is most likely due to the coordination of both a chelating carboxylate group. The asymmetric unit consists of two Mn$^{2+}$ ions, one Tpa and MI ligands are coordinated with DMF molecules (figure 2). The crystal structure includes, two types of manganese ions with different coordination environments. Manganese is coordinated with three oxygen atoms from three carboxylate groups and two...
Figure 3. (a) View of the coordination environment of Mn-MOF thermal ellipsoids are drawn at the 50% probability level. Oxygen molecules and hydrogen atoms have been omitted for clarity (symmetry codes: $1$-$1/2 + X, 1-Y, +Z; 2$-$1-X, 1-Y, 1-Z; 3$-$3/2-X, +Y, 1-Z$). The 1D right-handed helical chain of Mn-MOF. (b) A 2D layer composed of right-handed helical chains through O–H–O hydrogen bonds. (c) The 3D structure generated for Mn-MOF (black–C, blue–N, red–O, dark blue–Mn, white–H).
coordinated DMF molecules in an octahedral geometry. The Mn-MOF were anisotropic thermal parameters with refined on I2/a space group. Every hydrogen atoms were produced tentatively against the specific atoms and fixed thermal factors with refined anisotropy. It ought to be famous that solvent molecules in the structure were irregularly isolated and thus complicated to refine by discrete-atom models. This may be attributed to the bulky channels of ensuing in the puny contacts with uncoordinated DMF molecules, hence some atoms of DMF molecules with reduced thermal parameters are reserved and refined anisotropically. The figures 3(a)–(c) shows the packing crystal structures of Mn-MOF respectively.

3.2. FT-IR spectral analysis
Fourier transform infrared spectroscopy is an important technique to identify the presence of functional groups and or the interaction between the metal and organic ligands in [Mn(Tpa)(Mi)(Dmf)] samples. The FTIR spectrum is shown in figure 4. The broad absorption band centred at 3250–3000 cm$^{-1}$ is attributed for the existence of hydrogen-bonding connections within the frameworks. The presence of two strong peaks ranges at 1513 and 1369 cm$^{-1}$ could be ascribed for the mas(OCO) and ms(OCO) stretching vibrations of the Tpa. The aromatic nucleus [m(C–C), m(C–N)] are close to 1662 cm$^{-1}$, while m(C–H) bend vibrations are about 829 and 744 cm$^{-1}$ (phenyl) confirms the presence Mn–O bind. The shifting of the C=O of carboxylate and C–N vibrations indicate the formation of the bonding with the metal Mn centrally with the ligands Terephthalic acid and Methyl imidazole.
3.3. PXRD analysis

X-ray powder diffraction (PXRD) is a technique, which reveals the information about the nature of crystal structure and phase purity of the sample. The x-ray powder diffraction pattern (figure 5) shows the sharp peaks in the pattern, which indicates the crystalline nature of the material. The presence of prominent metallic peak at the 2θ values at 10.43 and 20.97 indicates the coordination of metal with the ligands to form complex. The pattern without much of noise and extra peaks hint us about the phase structure and purity of the products obtained. The theoretical (simulated) PXRD pattern calculated from the single-crystal XRD data is in good conformity with the experimental pattern. This conforms that the resulting phase is pure and highly crystalline. These results are consistent through the larger crystallite size and also an excellent crystalline nature can be seen.

3.4. FE-SEM analysis

The surface was characterized by using Field emission scanning electron microscope (FE-SEM) images of Mn-MOF. The FE-SEM imaging enables the study of the microstructure and surface morphology of the products. The micrographs show the particles distribution in a range of dimensions like diamond shaped crystals (figure 6). The FE-SEM images viewed under high and low (at 100 μm and 20 μm) magnifications. The images show the free particles of diamond-like crystals with attractive smooth surfaces.

3.5. EDX Analysis

Figure 7 is the EDX pattern of Mn-MOF. The EDX pattern confirms the presence of Manganese, carbon and oxygen along with their composition. The composition of the Element (weight %) is Carbon (48.84), Oxygen (26.20) and Manganese (24.97).
3.6. BET surface area measurement

The surface area, pore size and pore volume of Mn-MOF were evaluated via N2 adsorption using a NOVA-1000 BET surface area measurement instrument. Materials were degassed at 180 °C for 4 h. Surface areas of Mn-MOF were evaluated using nonlocal density functional theory (NLDFT). The BET specific surface area, pore textural properties, the cumulative pore volume, average pore diameter and the Langmuir specific surface area for the Mn-MOF were calculated. The sorption isotherms obtained with nitrogen gas signify type I isotherm with no hysteresis, which demonstrates the presence of microporous structure (figure 8). The obtained BET surface area is about 1.2352 m² g⁻¹, which represents the adsorption capacity of our compounds. The adsorption capacity reaches (the amount adsorbed) the value of about 8.760 m²/g⁻¹ and the average pore diameter of about 25.967 Å, which corresponds to micropore volume, 0.00569 cc/g.

3.7. Thermogravimetric analysis (TGA)

Thermogravimetric analysis for the compound measured under N2 atmosphere at a heating rate of 20 °C min⁻¹ without pre-treatment before the TG measurement is shown in the figure 9. The figure shows the weight loss at
two points. First weight loss observed between the temperature range of 250 °C–300 °C and the second weight loss observed between region 350 °C–450 °C. The first weight loss of about 18% in the range 250 °C and 300 °C can be due to the loss of free DMF molecule. The second weight loss of about 36% was observed between 350 °C–450 °C, which could be due to the removal of phenyl ring and carboxylate group. The Mn-MOF collected by heating the sample at 500 °C. After this no such weight loss observed till 600 °C. The solvent molecules were evaporated. The framework was started to disintegrate giving rise to an amorphous solid as a product. There was no functional group peak in figure, which shows the collapse of the compound because of evaporation of solvent molecules at 1000 °C. TGA curve of compound confirms the following points: (i) The Tpa molecules can be separated in the temperature range of 350 °C–450 °C (ii) The framework formulated as [Mn-MOF] is constant in the temperature range 350 °C–450 °C.

### 3.8. Photo luminescent properties

Luminescent complexes have arriving amazing attention in view of various potential applications, such as in chemical sensors, photochemistry, electroluminescent display, and so on. The solid-state luminescent emission properties of Mn-MOF at high temperature were investigated. The main emission peaks of Tpa and Mi are at 306 nm ($\lambda_{ex} = 442$ nm), 159 nm ($\lambda_{ex} = 488$ nm), and 552 ($\lambda_{ex} = 542$ nm), respectively, which can be assigned to the

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![Figure 8. N$_2$ adsorption–desorption isotherms of Mn-MOF compound.](image1)

![Figure 9. Thermo gravimetry(TG) curve for the Mn-MOF compound.](image2)
\[ \pi^* \rightarrow \pi \text{ or } \pi^* \rightarrow \pi \] transitions. Upon photo excitation, display the maximum emission peaks at 552 nm (\( \lambda_{\text{ex}} = 542 \text{ nm} \)), 159 nm (\( \lambda_{\text{ex}} = 488 \text{ nm} \)), respectively (figure 10). Comparing with the emissions of Tpa and Mi ligands, the emission bands of indicate significant blue/red shifts, which can be attributed to the charge transfer of Benzene-based ligands to Mn\(^{\text{II}}\) centers. The emission shoulder peak at 552 nm which is ascribed to the intraligand \( \pi^* \rightarrow \pi \) charge transfer. The different emission energies probably attributable to the different coordination configurations of ligand and the coordination environments around the Mn\(^{\text{II}}\) centers, which induce different HOMO-LUMO energy gaps. Luminescence displays obvious red shifts of Mn-MOF which should arise from the coexistence of the higher coordinated environments of Mn\(^{\text{II}}\) centers while exist in ligands. The differences in emission spectra associated with the different local environment around metal ions were also observed in other MOFs.

4. Electrochemical studies of Mn-MOF

4.1. Preparation of working electrode (Mn-MOF/BCPE):
A Mn-MOF sample, graphite powder and silicone oil binder (80 wt% or \( \sim 4 \text{ mg}, 15 \text{ wt\%} \) and 5 wt\% respectively) along with a drop of ethanol. This mixture was filled on teflon tube. Copper wire was used as a current collector. This electrode was left for drying at room temperature for about 24 h. The experimental setup in 5 mM K\(_4\)Fe(CN)\(_6\) and K\(_3\)Fe(CN)\(_6\) in 0.5 M KCl solution and buffer solution was used for cyclic voltammetry on electrochemical (CHI 608E) instrument. The saturated calomel electrode (SCE), platinum (foil) electrode and prepared Mn-MOF electrode were used as the reference, counter and working electrodes respectively [31].

4.2. Cyclic voltammetry study of Mn-MOF:
Figure 11 shows the cyclic voltammograms observed for the redox system of BCPE and Mn-MOF electrodes at the scan rate 50 mVs\(^{-1}\). A freshly prepared 10 mM of Potassium ferricyanide with 0.5 M Potassium chloride was placed in electrochemical cell [26, 27, 32, 33]. The following reactions are given below.

The BCPE electrodes of anodic and cathodic peak potentials were 0.26 V and 0.17 V respectively and the difference of redox peak potential (\( \Delta \text{Ep} \)) was 0.09 V. The anodic and cathodic peak potentials of Mn-MOF are 0.334 V and 0.098 V and the \( \Delta \text{Ep} \) is 0.23 V. The Mn-MOF electrode shows a significant enhancement in redox.
peak current compared to BCPE. In Mn-MOF shows a much higher anodic current from the electroactive Ferri/ Ferro system probe when it was exposed to the Mn-MOF comparison to the BCPE. These characteristics facilitate the transfer of electrons in the system by increasing the contact points of the electroactive probe with the electrocatalysis. This indicates a very good electrocatalytic activity of Mn-MOF \[28, 29\].

Figure 12 represents the cyclic voltammograms of Mn-MOF electrode at different scan rates \((10–100 \text{ mVs}^{-1})\). It is based on the redox interconversion of potassium ferrocyanide \((K_4[Fe(CN)]_6)\) to potassium ferricyanide \((K_3[Fe(CN)]_6)\) and vice versa. The ferrocyanide ion in aqueous solution is not stable and gets oxidized by oxygen dissolved in the solution. Therefore the more stable ferricyanide is used as a stock solution and the Fe(II) species are generated electrochemically \textit{in situ} by a pre-treatment. The oxidation and reduction peak currents are directly proportional to the scan rate which means that the reaction is surface restrained. These results indicate that the potentials of the oxidation peak and reduction peak shift to the positive direction and the negative direction respectively, which could be mainly due to the internal resistance of the electrode \[31, 34\].

4.3. Electrochemical detection of ascorbic acid (AA)
The electrochemical performance of Mn-MOF was studied by cyclic voltammetry (CV) technique using Mn-MOF-CPE electrode in phosphate buffer solution \((K_2HPO_4-KH_2PO_4)\) at pH 7.0. The Mn-MOF-CPE electrode
was correlated with bare carbon paste electrode (figure 13). The redox peaks with $E_{pa} = -0.524$ V and $E_{pc} = -0.912$ V appeared in the CV are accredited towards the $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox route. On the Mn-MOF, the oxidation of AA comprises a proton transfer process, and the oxidation potential of AA can be expressed as follows:

$$\text{AA}(\text{C}_6\text{H}_8\text{O}_6)\text{dehydroascorbate}(\text{C}_6\text{H}_8\text{O}_6)2\text{e}^- + 2\text{H}^+$$  \hspace{1cm} (3)

$$\text{Mn(III) - MOF} + \text{AA} \rightarrow \text{Mn(I)- MOF - AA}$$  \hspace{1cm} (4)

The ($\Delta E_p$) and half-wave potential values 0.388 V and 0.718 V respectively were calculated by using the following equation [35].

$$\frac{E}{2} = (E_{pa} + E_{pc})/2$$  \hspace{1cm} (5)

Ascorbic acid is a well-known vitamin by extreme significance innumerable biological diagnostics, biomedical, as well as pathological study reactions [36].

In figure 14, several cyclic voltammograms, obtained for different ascorbic acid concentrations, are presented. The peak corresponding to ascorbic acid oxidation appeared at 100 mV. The calibration graph obtained by cyclic voltammetry (figure 14) shows a linear range obtained between 0.25 and 1.25 mM.
ascorbic acid. The limit of detection and the limit of quantification were 0.085 mM and 0.28 mM respectively. Ascorbic acid is an electrically active by variously modified electrodes, but its oxidation implies adverse reduced selectivity and high overvoltage [37]. In sequence to attain capable electrodes for ascorbic acid recognition, the oxidation potentials must exist lowered and the selectivity has to be enhanced. demonstrates the CV respond of in PBS (pH − 7.0) through various concentrations of ascorbic acid (figure 14). The Mn-MOF-CPE oxidation peak of the current density values at $E_{pa} = 0.019 \text{ V}$, which is significantly lesser compared to earlier noted value is 0.360 V designed for the Mn-MOF-CPE modified electrode [38, 39]. The ascorbic acid concentration range was 0.25 mM to 1.25 mM. Mn-MOF-CPE current density is increased frequently. Sharp peaks were obtained for ascorbic acid.

Electrochemical behaviour of the Mn-MOF electrode was studied using buffer solution as a redox probe. Figure 14 shows the cyclic voltammogram of Mn-MOF. Using the same redox couple of buffer solution, the number of Mn-MOF particles deposited onto the graphite and the effective area of the Mn-MOF were estimated using the Randles–Sevcik equation (6) of a reversible process.

$$I_{pa} = (2.69 \times 10^5) \times n^{3/2} \times A_{ef} \times D^{1/2} \times n^{1/2} \times C_0$$

where $D$, $C_0$, $A_{ef}$ and $n$ are the diffusion coefficient, bulk concentration, effective area and the scan rate, respectively. Cyclic voltammetry experiments at different scan rates were performed with the Mn-MOF electrode in a solution of Phosphate buffer. From the plot of $I_{pa}$ versus $n^{1/2}$, a slope of $0.310 \text{ A V}^{-1/2} \text{ s}^{-1/2}$ was obtained.

From the D value of the solution, 2.82 for $n = 1$, the calculated value of Active surface area of the Mn-MOF electrode is $0.72 \times 10^{-10} \text{ cm}^2$. The geometrical surface area of the Mn-MOF electrode is 0.04 cm$^2$ according to randles sevcik equation.

The results specify that Ascorbic acid molecules must exist adsorbed over the outside of Mn-MOF-CPE and interrelate through the energetic slots in the structure initially. The Ascorbic acid oxidation is active while intermediaries to support the electron shift involving Mn-MOF-CPE and the Ascorbic acid [40–42]. The ascorbic acid peak potential is a great deal nearer to the Mn-MOF-CPE peak potential is $0.72 \text{ V}$, which is significantly lower compared to the earlier noted value.

5. Conclusions

A new Mn-MOF [Mn(Tpa)(Mi)(DMF)] successfully synthesized using terephthalic acid, methylimidazole ligands by the solvothermal method at low temperature at about 120 °C. The accelerated synthesis of crystals has been observed in solvothermal method and it could be due to the fast nucleation reaction whereas, in a conventional heating method, the nucleation takes place only on the walls of the reaction container. But solvothermal method provides a uniform nucleation environment for the crystal growth. The SEM images have shown a very attractive morphology of the product and dimensions of thermange 100 μm and 20 μm. The surface area of 1.235 m$^2$ g$^{-1}$ and pore volume of 0.00569 cc g$^{-1}$ of the MOF were unravelled from the various techniques as discussed in the text. Also the Mn-MOF provides rich active sites and an outstanding electrochemical activity for ascorbic acid detection [43, 46].

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