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Synthesis, Characterization and Catalytic Potency of Zn-based MOF for Knoevenagel Condensation Reaction

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Abstract: ***A Zn based metal organic framework with pyridine 2, 5-dicarboxylate (Zn-based MOF) were prepared as a reusable heterogeneous catalyst using solvothermal method. Zn-based MOF was used as heterogeneous catalyst for synthesis 5-arylidene malononitrile in ethanol under reflux condition. The attractive features of present method are mild reaction condition, short reaction time, simplicity, easy separation of catalyst and excellent yield.***
Keywords: Metal organic framework, heterogeneous catalyst, solvothermal method.

I. INTRODUCTION

Metal organic framework (MOF) represents designable, crystalline mesoporous materials that are constructed from linking inorganic metal ions or cluster by organic chain binding with strong bond [1-4]. As a result of their tunable pore size, large surface area, high thermal and good chemical stability and high density of active sites either inorganic metal cluster, organic linker or both due to this reason offers MOF tremendous opportunities for use as heterogeneous catalyst for organic transformation[5]. As a part of our interest in this area, we have designed Zn based MOF heterogeneous catalyst and and characterized by powder-X ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDAX), Brunauer-Emmer-Teller surface area analysis (BET). The synthesized and characterized Zn-based MOF is used as heterogeneous catalyst for efficient synthesis of 5-arylidene malononitrile derivatives.

It is one of the most versatile C-C bonds forming reaction in organic synthesis. Knoevenagel condensation of benzaldehyde and malononitrle to obtains 5-arylidene malononitriles which has found many applications such as commercial compound of antimalarial drug lumifantrine an integrant of coartem and synthesis of intermediate of fine chemicals, in the synthesis of intermediate like Imidazopyridine, Quinoline, Benzofuran, Coumarin derivatives of biologically and pharmaceutically active compound [6-9]. Knoevenagel condensation reaction has been enormous used in synthesis of coumarin and their derivatives an elevated group of organic product consumption as additives to food and cosmetics.

II. MATERIALS AND METHODS

A. Chemical and Instrumentation

All solvent and chemical were of analytical grade and purchased from Merck, Spectrochem and HPLC and Absolute and used as such FT-IR Spectra were recorded by using ATR on Bruker instrument . PXRD patterns were recorded by D_8 advance Bruker X-ray diffractometer using monochromatic Cu-Kα radiation (λ= 1.5405 A°). ^{1}H and ^{13}C NMR spectra were recorded on 400 MH_Z FT-NMR spectrometer in DMSO as solvent .HRMS was measured in positive ionization mode on an Agilent 6520 (Q-TOF) mass spectrometer. Scanning electron microscope was performed on JSM-6390 operated. The surface area was calculated by using Brunauer- Emmett-Teller N_2 sorption isothermal quanta chrome instrument.

B. Preparation of the Zn-based MOF

Zinc nitrate hexahydrate (2.359 gm) and Pyridine 2,5- dicarboxylic acid (H_2pdc) (0.509 gm) were dissolved separately in 30 ml DMF and 10 ml ethanol. These clear solutions of H_2pdc were added in zinc nitrate solution drop wise with constant stirring for 15 min. The mixture was added in 100 ml Teflon linked autoclave. The system was sealed and heated at 130°C under autogeneous pressure for 24 h. After completion of the reaction product were cooled at RT. The resulting crystal were collected by filtering and then washed with DMF and dried at room temp. The dried crystals were immersed in methanol for 2 days. The fresh methanol was added at every 12h. Solvent was decanted and dried under vacuum in vacuum desiccators. Solid product was prepared Zn based MOF catalyst, characterized and used as a catalyst.

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C. General Procedure for the Synthesis of 5-arylidene Malononitrile

A mixture of aromatic aldehydes (1 mmol), malononitrile (1 mmol) with a catalyst IRMOF-3 (40 mg) was reflux in ethanol (5ml) with constant stirring for the specified time mentioned in **Table 3**. The progress of the reaction was monitored by TLC (petroleum ether: ethyl acetate = 7:3 as eluent). After completion of the reaction, the mixture was poured in crushed ice. The crude product was obtained, crude product dissolved in hot ethanol.The catalyst is insoluble in ethanol; thus catalyst was separate out easy by simple filtration. The filtrate was concentrated and the crude product obtained was recrystallized from ethanol to afford pure product (3a-k).

D. Spectral Data of Representative Sample

5-Benzylidenemalononitrile (3a):

^{1}HNMR (DMSO-d_6): δ 7.61-7.64 (m, 2H) 7.68-7.71 (m, 1H), 7.94-7.96 (m,2H) 8.55 (s, 1H). ^{13}C NMR (DMSO-d_6): 81.47, 113.04, 129.38, 131.15, 163.43. FT-IR (ATR, ν cm^{-1}): 2360, 2341, 1580, 1548. HRMS: M^{-1}, 155.06

III. RESULT AND DISCUSSION

A. XRD Analysis

The X-ray diffraction pattern of Zn-based MOF depicted in Fig. 1 shows intense peaks at 2θ = 24.50, 27.62, 31.35, 35.27 with corresponding planes (112), (330), (421), (520) respectively (JCPDS Id no. 47-2088 PDF # 472088, volume (CD)- 882.5), which are characteristic peaks found tetragonal phase of Zn-based MOF material. On the other hand, comparison of diffraction pattern of the fresh with recovered Zn-based MOF catalyst that the crystallinity and integrity of the catalyst is maintained during the organic transformation.

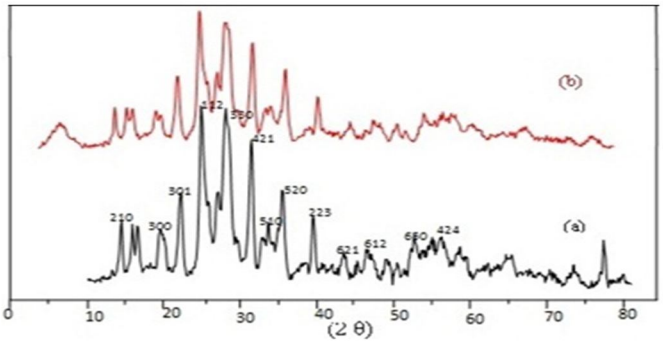


Fig. 1. Powder X-ray diffraction pattern of Zn-based MOF catalyst. (a) Newly prepared (black) (b) Used four time for 3a (red).

B. FT-IR analysis

Infrared spectroscopy analysis provided the valuable information considering the nature of functional group coordinated to the metal ion. The selected IR spectrum data of the pyridine 2,5 -dicarboxylic acid ligand and Zn-based MOF, are summarized in Table.1, onto comparisons the absorption band at 1716 to 1695 cm^{-1} is due to C=O group of pyridine 2,5 dicarboxylic acid.

The absorption band of Zn-based MOF was observed in the range 1651 to 1609 cm^{-1}, which confirmed the C=O group of pyridine 2,5 dicarboxilic acid coordination with Zn metal ion. The C=C and C=N stretching frequency were found in the range 1386-1285 cm-^{1} and 1149-1050 cm^{-1} but it reduce 1116-1033 and 1358-1280 cm^{-1} in Zn-based MOF.

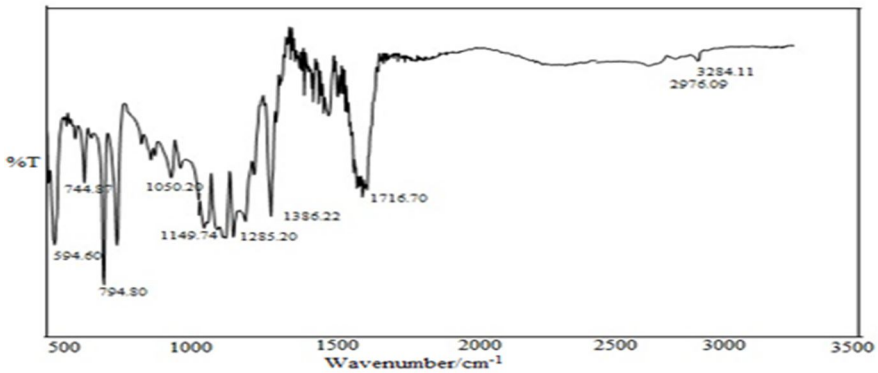


Fig. 2. FT-IR Spectrum pyridine 2,5- dicarboxylic acid ligand.

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Table 1. Selected FT-IR frequencies (cm^{-1}) of the Pyridine- 2,5 dicarboxylic acid and Zn-based MOF

Ligand/MOF	$\nu_{(C=O)}$	$\nu_{(C=N)}$	$\nu_{(C=C)}$
H_2pdc Ligand	1716	1386	1149
Zn based MOF	1609	1358	1116

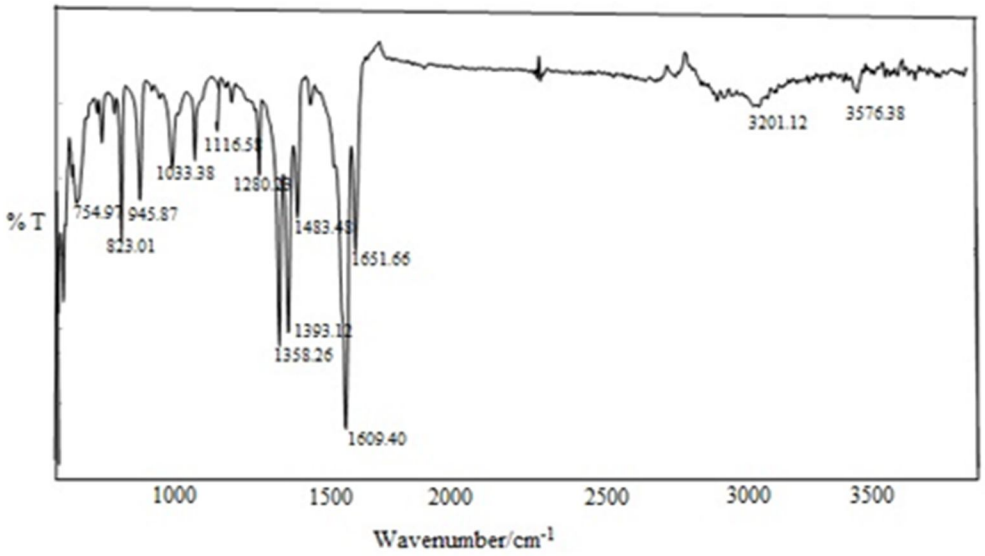


Fig.2a. FT-IR spectrum of Zn-based MOF catalyst.

C. TGA Analysis

Thermo gravimetric analysis was defined for the conformation of thermal stability of synthesized Zn-based MOF material. The TGA analysis curve shows two major weight losses as shown in Figure.3. The first 36% weight loss was observed in the range 350°C to 450°C it may due to the evaporation of lattice water molecule from Zn-based MOF. The second 59.57% weight loss was found in the range 550 °C to 850 °C , it conform the elimination of pyridine 2,5- dicarboxylate linker of Zn-based MOF. It has been found that the Zn-based MOF catalyst shows good thermal stability up to 550°C.

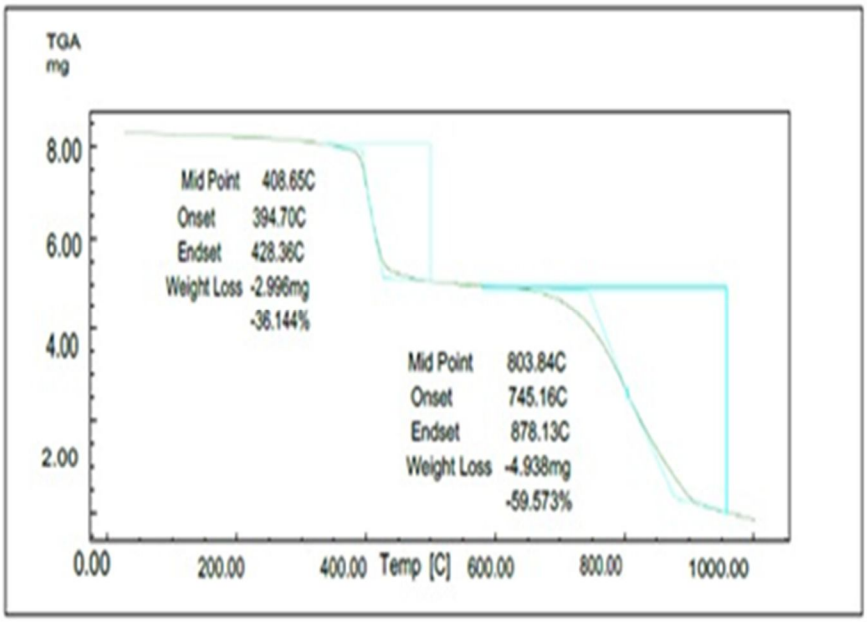


Fig. 3. TGA analysis of Zn- based MOF.

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D. BET Analysis

The BET surface area, average pore diameter and pore volume of Zn-based MOF were found to be 189.29m^2/g, 53.36 A^o and 0.503cm^2g^{-1} respectively calculated by the N_2 absorption desorption BJH isotherm.

E. SEM Analysis and EDS Analysis

The surface morphology of the Zn-based MOF catalyst have been studied by scanning electron microscopy (SEM), which basically show uniform spherical flower crystalline arrangement, as shown in fig.4. The element composition of Zn-based MOF is shown in fig.5, which shows the presence of zinc (11.22%), carbon (51.45%), oxygen (35.92%), (F (0.90%), Cu (0.52%) trace amount analyzed impurity) respectively. The EDS profile of Zn-based MOF catalyst confirms presence of the zinc, carbon, oxygen element.

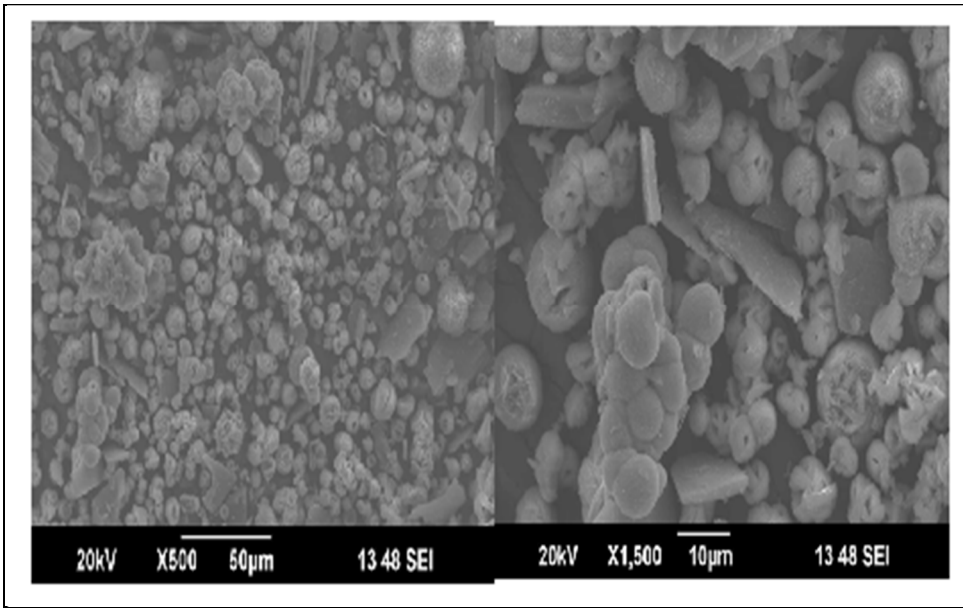


Fig. 4. SEM image of Zn-based MOF catalyst.

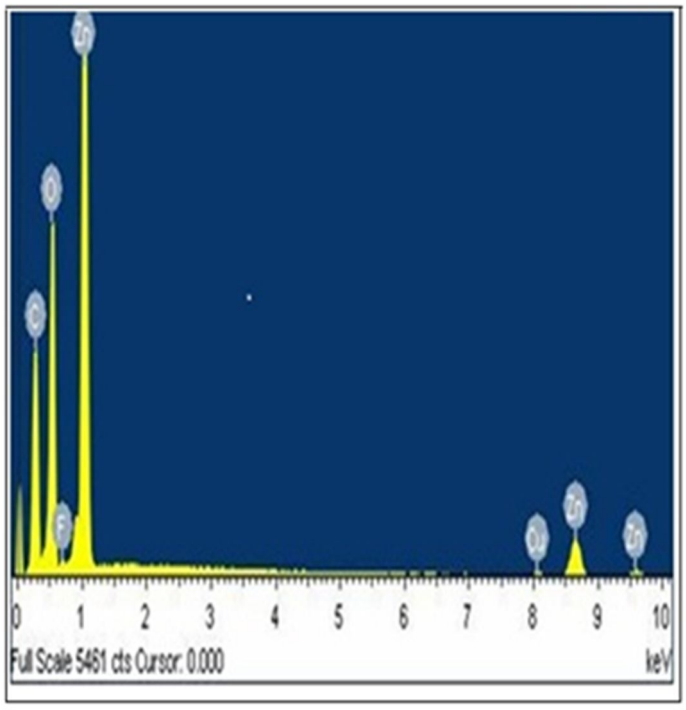


Fig.5. EDAX spectrum of Zn-based MOF catalyst.

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F. Optimization of Reaction Condition

To optimize the suitable reaction conditions, benzadehyde (1 mmol), was react with malononitrile (1 mmol) as model reaction with different amount of synthetic Zn based MOF as catalyst in various solvents at reflux condition and results are summarized in (Table 2). In the absence of catalyst the reaction does not give satisfactory yield of product (3a) after 90 min. The same reaction when carried out with different amounts Zn based MOF of under reflux condition and it has been found that reaction gave excellent yield of product (3a) in 20 minutes which indicate important role of Zn based MOF catalyst. Furthermore, the amount of catalyst was optimized on sample reaction and it has been observed that 40mg of Zn based MOF is suitable to catalyze reaction smoothly. On the basic of optimization of the catalyst, Studies on effect of the different like protic and aprotic solvents were tested and when reaction carried out in protic solvent such as ethanol and acetonitrile, it gave maximum yield in reduced time as compared to non protic solvents such as DCM, toulene which gave lower yield (Table 2)

Table 2. Effect of various solvent on the model reaction 3a in the presence of Zn-based MOF catalyst.

Entery	Solvent	Catalyst (mg)	Time (min)	Yield (%)[a]
1	DCM	40	40	69
2	Tolulene	40	30	70
3	DMF	40	35	65
4	CH_3CN	40	30	75
5	Ethanol	----	90	40
6	Ethanol	10	20	90
7	Ethanol	20	20	93
8	Ethanol	40	20	98

In order to examine the scope and efficiency of the present method, substituted benzaldehydes with malononitrile were tested under optimum reaction conditions and it was observed that no significance effect on the yield of corresponding 5-arylidene malononitrile derivaties for different substituented aromatic aldehyde in stipulated time (**Table 3)**. The efforts have been made towards the recovery and reusability of the catalyst. The catalyst was separated after the completion of reaction. After completion of reaction, the reaction mixture was dissolved in hot ethanol and filtration. The recovered catalyst was washed 3 to 4 time with DMF then immersed in methanol 24 h and activated by drying at 130^{o}C for 3 hour, before the next catalytic run.

Table 3. Synthesis of 5-arylidene malononitrile derivatives using Zn-based MOF catalyst

Sr.No.	Ar-CHO	Entry	Time (min)	Yield (%)[a]	Melting Point (^{o}C)	
					Observed	Found [lit.]
1	C_6H_5	3a	20	97	82-84	83-84
2	4-$CH_3C_6H_4$	3b	25	95	127-128	128-129
3	4-$NO_2C_6H_4$	3c	30	94	162-163	161-162
4	4-OHC_6H_4	3d	25	97	186-188	187-188
5	4-ClC_6H_4	3e	30	92	158-159	158-160
6	4-OCH3C_6H_4	3f	20	94	112-114	113-114
7	3-OHC_6H_4	3g	23	92	90-91	91-92
8	2-ClC_6H_4	3h	25	90	95-96	94-95
9	2-Furyl	3i	30	90	64-65	65-66
10	3-$NO_2C_6H_4$	3j	25	93	141-143	140-142
11	2-OHC_6H_4	3k	24	91	162-163	163-164

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IV. CONCLUSION

In summary , use of Zn-based MOF as reusable catalyst is proved to be effective for the synthesis of 5-arylidene malononitriles derivatives. Zn-based catalyst was found that the good catalytic activity up to four run with excellent yield of desired product in less time. This protocol offer several advantages such as reasonable reaction time, mild reaction condition, simple work up, high yield of desired product, high reusability.

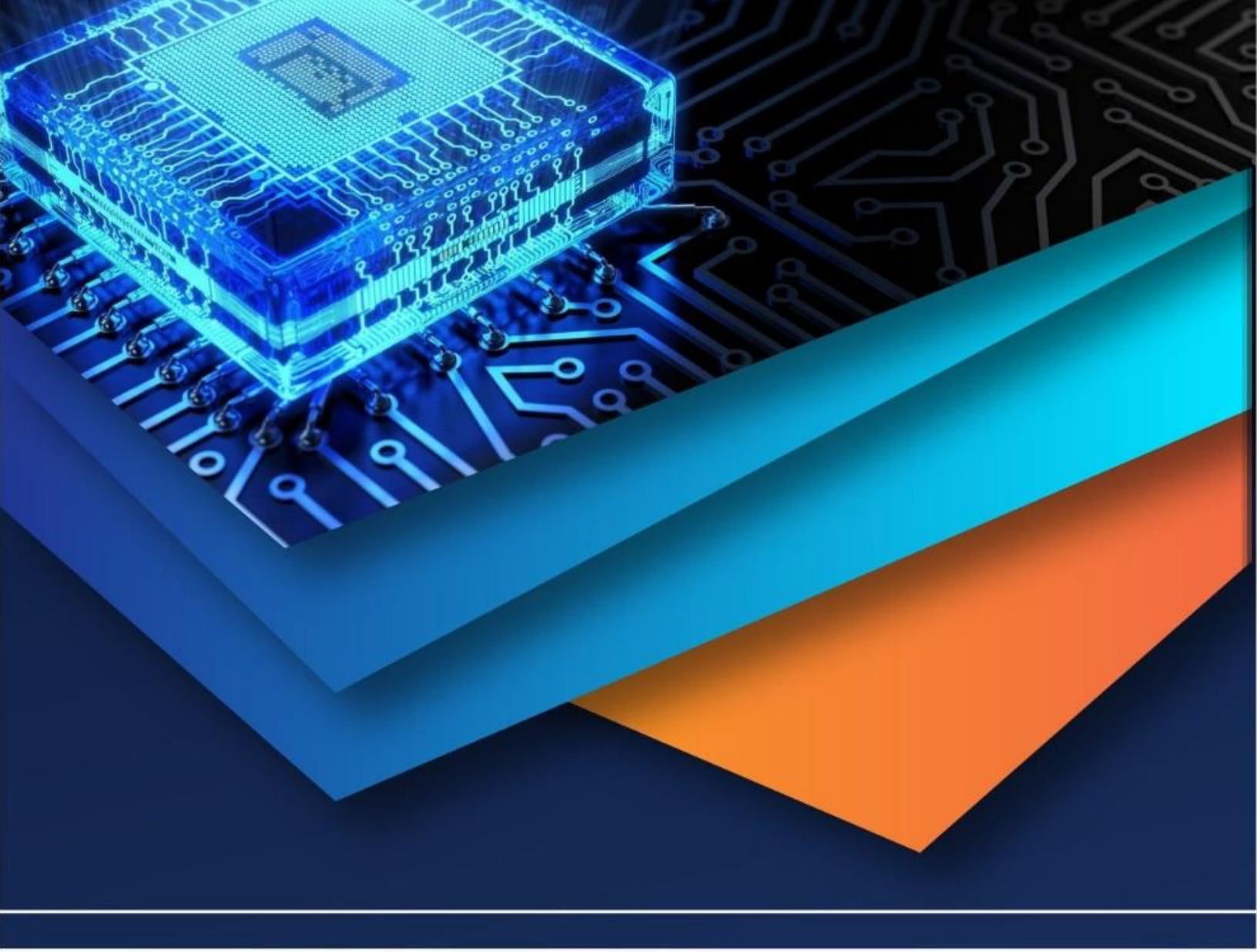
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