# **Inorganic Chemistry**

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# Zn(II)/Cd(II)-Based Metal–Organic Frameworks as Bifunctional Materials for Dye Scavenging and Catalysis of Fructose/Glucose to 5-Hydroxymethylfurfural

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ABSTRACT: Fu (MOFs) {[M(50	inctional neutral metal—orga $\mathbf{P}$ $\mathbf{P}$	anic frameworks ADES-4: Cd(II)	5 Ads	orption			

(MOFs)  $\{[M(5OH-IP)(L)]\}_n [M = Zn(II) \text{ for ADES-4; Cd(II)} \text{ for ADES-5; 5OH-IP} = 5-hydroxyisophthalate; L = <math>(E)$ -N'-(pyridin-3-ylmethylene)nicotinohydrazide) have been synthesized by a diffusion/conventional reflux/mechanochemical method and characterized by various analytical techniques. Crystals were harvested by a diffusion method, and single-crystal X-ray diffraction (SXRD) analysis revealed that an adjacent  $[M_2(COO)_2]_n$  ladder chain generates isostructural two-dimensional network motifs by doubly pillaring via L. The bulk-phase purity of ADES-4 and ADES-5 synthesized by a versatile synthetic approach has been recognized by the decent match of powder X-ray diffraction patterns with the simulated one. Both ADES-4 and



ADES-5 showed selective adsorption of cationic dyes methylene blue (MB), methyl violet (MV), and rhodamine B (RhB) over anionic dye methyl orange (MO) from water with good uptake and rapid adsorption. Utilization of ADES-4 as a chromatographic column filler for adsorptive removal of individual cationic dyes as well as a mixture of dyes has been demonstrated from the aqueous phase. Interestingly, ADES-4 is reusable with good stability, and it showed a dye desorption phenomenon in methanol. The probable mechanism of cationic dye removal based on insight from structural information and plausible supramolecular interactions has also been explored. Both MOFs also showed efficient catalytic transformation of fructose and glucose into the high-value chemical intermediate 5-hydroxymethylfurfural of industrial significance.

# ■ INTRODUCTION

Design and fabrication of metal-organic frameworks (MOFs), an inorganic/organic hybrid material governed by a selfassembly process of organic linkers and metal nodes as building blocks possessing high surface area/porosity, offer diverse applications as a functional material as well as academic interest. Tunable and desired properties of MOFs can be realized by the sensible selection of functionally decorated ligand moieties and the metal nodes.<sup>1,2</sup> Further, unique features of MOFs such as chemical/thermal stability, robustness, topologies, and interesting surface chemistry indicate a versatile material platform with a plethora of applications in diverse areas such as chemical probes, magnetism, gas sorption/separation, catalysis, etc.<sup>3-11</sup> With inherent features such as controllable pore environment, designable channel size, and high specific surface area, MOFs have become celebrated candidates for the removal and sensing of chemical pollutants.<sup>12-15</sup> Functional decoration of the ligand moiety as linkers that can allow supramolecular interactions with pollutants along with the above-mentioned attributes support MOFs as efficient adsorbent materials for hazardous chemicals. Sensing and effective removal of organic contaminants, particularly dye molecules from industries/water bodies, remain a current research interest by academia and industries due to its environmental significance and impact on human health. General strategies adopted for wastewater treatment out of the pollutants rely on adsorption, coagulation methods, as well as membrane filtration and ion-exchange techniques, etc.  $^{12-15}$ 

Dyes are industrially important colorants widely used in paper, textiles, and the plastics industries, and the release of the unprocessed colored water is one of the main sources of environment pollution. The textile industry severely pollutes water bodies by discharging large amounts of synthetic dyes as effluent after industrial use due to inefficient dyeing processes. Therefore, effective elimination of synthetic dyes from wastewater is a challenging topic for scientists and academics.

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For sustainable growth and mitigating water pollution, development of new smart materials with efficient reversible dye adsorptive removal with good recyclability has great promise with real-world applications. Besides, traditional porous functional materials such as zeolite, charcoal, activated carbon, etc., MOFs have been receiving much attention as adsorbents for hazardous molecules including dyes in recent years.<sup>16-25</sup> The primary requirement for MOF as a dve adsorbent is the thermodynamic stability of the MOF in aqueous dye solutions. The mechanistic aspects of dye adsorption on MOF surfaces mainly hinge on various inherent elements such as porosity and pore geometry, MOF linkers with specific functional groups, and suitable donor-acceptor pairs for hydrogen-bonding interactions of the framework and dye molecules. Moreover, the charge of dye and adsorbent material also plays a crucial role in governing the dye adsorption phenomenon. For example, anionic frameworks tend to adsorb cationic dyes and vice versa, and neutral frameworks can show selectivity for dyes of either charge, recognized by various noncovalent interactions such as hydrogen bonding,  $\pi \cdots \pi$  stacking, as well as pore dimensions and steric factors.<sup>26-28</sup> Hence, MOFs as celebrated materials have been used for adsorptive removal/separation of dyes from wastewater/textile effluent due to their tunable structureproperty features.

Alternatively, MOFs are also well-known for their heterogeneous and recyclable catalytic properties for chemical productions based on their high surface area, tunable pore sizes, abundant Lewis/Brønsted acid/base sites, and controllable structures. Catalytic transformation of fructose and glucose into high-value chemical intermediates including 5hydroxymethylfurfural (HMF) is one of the important reactions with industrial significance. HMF is a promising building block for chemical industries, and the selective C6 sugar-to-HMF catalytic transformation is an industrially important reaction in the context of sustainable development. HMF is a versatile intermediate in the production of valueadded chemicals such as alternative fuels, diesel fuel additives, industrial solvents, bioderived polymers, etc. A typical strategy for the synthesis of HMF is the dehydration reaction of fructose/glucose using a variety of catalytic materials such as metal complexes and oxides, metal halides, ion-exchange resins, zeolites, functionalized carbonaceous materials, functionalized mesoporous materials, acidic ionic liquids (ILs) including organic inorganic acids, etc.<sup>29–33</sup> The main drawback for some of these catalytic systems such as equipment corrosion and difficult product isolation, low product yield, longer reaction times in the case of solid acid catalysts, and the low thermal stability of the resin-based catalysts hampering reaction efficiency. Even though a handful of MOF-based catalysts for fructose to HMF production is available in the literature, the design and development of stable and efficient catalysts are in demand considering the industrial importance of HMF.<sup>34–41</sup> MOFs with a highly porous and ordered nature with coordinatively unsaturated metal sites and an organic ligand component with inherent functional groups or the introduction of desired functional groups into MOFs through postsynthetic modification (PSM) can probably promote substrate transfer within the MOF catalyst in facilitating HMF production by an efficient catalytic reaction.

Our research activities are focused on the design, synthesis, and practical utility of mixed-ligand MOFs/luminescent MOFs (LMOFs) as heterogeneous catalysts for CO<sub>2</sub> sequestration

and selective detection/sensing of hazardous pollutants.<sup>9,42-47</sup> Herein, we synthesized two water-stable, isostructural mixedligand two-dimensional (2D) MOFs  $\{[Zn(5OH-IP)(L)]\}_{n}$ (ADES-4) and {[Cd(5OH-IP)(L)]}, (ADES-5) involving (E)-N'-(pyridin-3-ylmethylene)nicotinohydrazide) (L) and 5hydroxyisophthalic acid (5OH-H<sub>2</sub>IP) as ligands. Both MOFs were crystallized by the self-assembly of 5OH-IP and L with the respective metal salt in a MeOH/H2O medium by slow diffusion at room temperature, and the bulk phase-pure materials were synthesized by different routes. The present work reports on the preparation and comprehensive characterization of two isostructural MOFs, by various physicochemical methods as well as SXRD analysis. The application of these smart materials toward reversible adsorptive removal of dyes and recyclable heterogeneous catalysts for the conversion of C6 sugar to high-value chemical intermediate HMF under moderate reaction conditions is discussed.

# RESULTS AND DISCUSSION

Characterization of ADES-4 and ADES-5. Crystals and bulk phase-pure product of the isostructural compounds ADES-4 and ADES-5 obtained by different methods have been characterized by SXRD analysis and various physicochemical methods. The experimental PXRD profile of the synthesized materials is in good agreement with SXRD patterns of the crystals establishing the bulk phase purity of both MOFs (Figure S1). Further, detailed characterization of both MOFs was established from experimental data such as FTIR, TGA, SXRD, and elemental analysis. Both MOFs revealed numerous characteristic absorption bands of (E)-N'-(pyridin-3-ylmethylene)nicotinohydrazide) (L) and the corresponding dicarboxylate anion in the FTIR spectra. The presence of carboxylate groups appearing as strong bands at 1545 and 1390  $\text{cm}^{-1}$  for ADES-4 and at 1554 and 1379  $\text{cm}^{-1}$ for ADES-5 respectively can be ascribed to the  $\nu$ (COO)<sub>as</sub> and  $\nu$ (COO)<sub>s</sub> vibrations. The difference in carbonyl symmetric and antisymmetric stretching frequencies  $\Delta \nu = 155$  and 175 cm<sup>-1</sup> indicates the carboxylate moieties with chelating and bidentate coordination modes in MOFs. The amide N-H and C=O bands of L appeared at 3197 (w) and 1666  $\text{cm}^{-1}$  (s) for ADES-4 and at 3203 (w) and 1667  $\text{cm}^{-1}$  (s) for ADES-5, which were observed at 3202 and 1676  $cm^{-1}$  in the free ligand L (Figure S2).<sup>46</sup> The red shift of the N-H bands in the spectra of the MOFs can be explained by the formation of N-H--O hydrogen bonds between the amide functionality of L with dicarboxylate oxygen atoms as observed from SXRD analysis. The nonbonded hydroxyl stretching frequency of 5OH-IP appeared as broad medium bands at 3421 and 3423 cm<sup>-1</sup> corresponding to ADES-4 and ADES-5. Thermal and chemical stability is a highly desirable property of MOFs toward practical applications. As depicted in Figure S3, TGA data revealed good thermal stability for both MOFs, and the degradation of the organic ligand moiety followed by the structural decomposition commences after 350 °C in both cases. Further, the hydrolytic stability of both MOFs was also established by PXRD data of the dried, recovered MOF material soaked in water for 72 h, showing an identical pattern with simulated PXRD data (Figure S1). The chemical stability of ADES-4 in MeOH and DMSO solvent was also check by dispersing the MOF material in the respective solvent for 72 h as well as refluxing for 24 h in the case of DMSO, and the PXRD patterns of recovered materials matched well with simulated PXRD data confirming the stability of the material in



Figure 1. (a) Linker coordination with Zn(II) metal in ADES-4; (b) one-dimensional metal-carboxylate chain showing  $[Zn_2(COO)_2]$  SBU of ADES-4; (c) pillared-layered 2D network in ADES-4; (d) overall supramolecular framework of ADES-4 in an ABAB manner.

these organic solvents (Figure S1). Good chemical and thermal stability of both MOFs can be indicated due to a robust double-pillared network along with strong supramolecular interactions between the 2D nets witnessed in SXRD analysis.

Crystal Structure of  $\{[Zn(5OH-IP)(L)]\}_n$  (ADES-4) and {[Cd(5OH-IP)(L)]}<sub>n</sub> (ADES-5). SXRD analysis of two isostructural mixed-ligand Zn(II)/Cd(II) 2D metal-organic frameworks (ADES-4 and ADES-5) based on (E)-N'-(pyridin-3ylmethylene)nicotinohydrazide) (L) and 5-hydroxyisophthalic acid (50H-H<sub>2</sub>IP) harvested by a diffusion method has been investigated. Crystallographic refinement parameters and selected bond lengths/angles for both the MOFs are summarized as Tables S1 and S2 in Supporting Information. Crystallographic studies determined that both ADES-4 and ADES-5 are isostructural with a 2D framework in which the  $Zn^{2+}/Cd^{2+}$  nodes are linked by **5OH-IP** generating a ladder chain motif which is doubly pillared by the Schiff base ligand L. Asymmetric units of both MOFs are constituted by a central metal ion  $(M^{2+})$  along with one molecule each of **5OH-IP** and L respectively (Figure 1a and Figure S4a). Highly distorted octahedral geometry with N<sub>2</sub>O<sub>4</sub> coordination around each M<sup>2+</sup> is provided by four carboxylate oxygens from three different 5OH-IP and axially pillared nitrogen from two Schiff base ligands. As shown in Figure 1b (Figure S4b), each 5OH-IP is engaged in a  $\mu_3 - \eta^2 \eta^1 \eta^1$  bridging mode through the carboxylate oxygen with the  $M^{2+}$  to generate a binuclear  $[M_2(COO)_2]$ secondary building block (SBU) extending in the formation of a one-dimensional ladder chain. L adopts a  $\mu_2$ -bridging mode via terminal pyridine nitrogen of L with the adjacent  $[M_2(COO)_2]_n$  1D chains oriented along the *b*-axis generating a doubly pillared 2D network as depicted in Figure 1c (Figure S4c). The M···M distance within the dimeric cluster is 4.18/ 4.02 Å, and between the nearest  $[M_2(COO)_2]$  secondary building block (SBU) bridged by symmetrically disposed 5OH-IP is 7.41/8.26 Å for ADES-4 and ADES-5 respectively. The M…M distance between the ladder chains doubly bridged by the N-donor ligand L is 14.44/14.73 Å respectively in the isostructural MOFs.

Pyridyl rings of the L doubly pillared with the metal centers are engaged in  $\pi \cdots \pi$  stacking, and the centroid  $\cdots$  centroid (Cg1…Cg2) separation distance of the pyridyl rings is 3.87 Å in ADES-4 and 3.70 Å in ADES-5 (Figure S5). In an attempt to understand the supramolecular interactions, we have analyzed the hydrogen bonding in detail. The packing diagram revealed that the two-dimensional nets are oriented almost diagonal to the ac-plane, and the offset stacked 2D alternate nets are involved in effective and identical hydrogen-bonding interactions in the supramolecular assembly of both MOFs (Figure 1d and Figure S4d). Subsequently, amide hydrogen (H3C/H2C) of the Schiff base ligand in the respective MOF ADES-4/ADES-5 is involved in strong N-H…O interactions as a donor with the carboxylate oxygen (O5/O4), and the phenolic hydrogen of the 5OH-IP (H4C/H3C) is involved in  $O-H\cdots O$  contact with the amide oxygen (O6/O6) as an acceptor in linking the offset 2D nets. In addition to this, the phenyl hydrogen of 5OH-IP (H7/H7) makes good intermolecular C-H···O contact in both the MOFs with the carboxylate oxygen (O4/O5) in stabilizing the molecule in the crystal lattice (Figure S5). Details of all hydrogen-bonding interactions with their symmetry codes are provided in Table S3 of the Supporting Information.

Dye Adsorption Studies in the Aqueous Phase Using the MOFs. Recently, diverse methods for the treatment of industrial wastewater for removal of dyes, have been proposed such as adsorption, membrane filtration, and photocatalysis, etc. High stability of dye stuffs hampers the degradation process by oxidants/irradiation, and adsorption is one of the efficient processes for the removal of organic dye moieties from wastewater due to its simplicity, high efficiency, and costeffectiveness. Because of the good water stability, high specific surface areas/porosity, and presence of functionally decorated ligands for supramolecular interactions, MOFs are also in the limelight for wastewater treatment to adsorb pollutants including organic dyes. Typical features such as ionic interactions, electrostatic interactions, supramolecular interactions, size exclusiveness, and the nature and charge of the

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MOFs play a major role in absorptive removal process. For example, the cationic/anionic nature of the MOFs are wellknown for their selectivity toward anionic or cationic dyes by ion exchange, guest exchange, and/or host-guest interactions. Dye adsorption properties of the neutral framework is comparatively scant in the literature, and the present study comprised highly water-stable and functionally decorated neutral 2D Zn/Cd-based MOFs and their reversible adsorptive removal properties of dye molecules.<sup>48-56</sup> To investigate the efficiency for aqueous phase dye removal, we chose three positively charged dyes, methylene blue (MB), methyl violet (MV), rhodamine B (RhB), and a negatively charged dye, methyl orange (MO), as model pollutants for removal experiments by ADES-4 and ADES-5 possessing acylamide and hydroxyl functional groups in the dual ligand moiety (Scheme 1).





Considering the environmentally friendly nature of Zn-MOFs, all the systematic dye adsorption studies mainly focused on using ADES-4, and the final optimized condition was applied in the case of isostructural Cd-based ADES-5 for the comparative study. In an attempt to check the initial adsorptive removal capacity, 100 mg of the MOF material was added to 10 mL of aqueous solution of the individual dye (5  $\times$  $10^{-5}$  M) and mixed thoroughly for 3 h at RT with constant stirring under dark conditions. A major reduction in color intensity was observed in the case of all cationic dye molecules, while maintaining almost intact color intensity in the case of anionic MO after 3 h in the presence of MOF adsorbent (Figure 2a-h). The reduction in color intensity observed by the naked eye clearly demonstrates that mainly cationic dyes (MB and MV) were adsorbed by the MOF with an edge for MB from this series. This is also reflected in the color transformation of pristine off-white MOFs to blue, violet, pink, and light orange, in the presence of the respective dyes MB, MV, RhB, and MO, for the dye-adsorbed material ADES-4@ dye where (dye = MB, MV, RhB, or MO) (Figure 2i). The dye adsorption experiment was performed and monitored using UV-vis spectrometry to evaluate the decrease in dye concentration. The absorbance maxima of the corresponding

dyes MB ( $\sim$ 664 nm), MV ( $\sim$ 588 nm), RhB ( $\sim$ 556 nm), and MO ( $\sim$ 464 nm) were monitored in UV–vis studies to check the drop in dye concentration by adsorption of the MOF (Figure 2a–h).

The initial set dye concentration  $(5 \times 10^{-5} \text{ M})$  was dropped to  $1.43 \times 10^{-5}$ ,  $1.74 \times 10^{-5}$ ,  $3.67 \times 10^{-5}$ , and  $4.78 \times 10^{-5}$  M respectively for, MB, MV, RhB, and MO at the equilibrium concentration after 3 h of constant stirring in the aqueous phase in the presence of ADES-4. Almost the same trend in the drop of dve concentration was observed in the case of ADES-5 also, and the observed concentration drop for MB, MV, RhB, and MO was  $1.44 \times 10^{-5}$ ,  $1.61 \times 10^{-5}$ ,  $3.79 \times 10^{-5}$ , and  $4.80 \times 10^{-5}$  $10^{-5}$  M, respectively. The adsorption capacity of both MOFs for the respective dyes is in order of MB > MV > RhB > MO, and the dye removal percentage  $(\eta)$  calculated for MB, MV, RhB, and MO correspond to ~71%, 65%, 27%, and 5%, by ADES-4 and 71%, 68%, 24%, and 4% by ADES-5 (eq S1). These results clearly indicate that cationic dyes were showing more adsorption affinity by the MOFs compared to the negligible adsorption of the anionic dye MO. Calibration curves of the corresponding dyes using standard aqueous solutions were performed to estimate the absorbed amount of dye by the MOF in a selected time period (Figure S6). Adsorptive removal amounts of the individual dyes (mg/g) by ADES-4 were found to be 1.14, 1.39, 0.63, and 0.072 and by ADES-5 1.13, 1.38, 0.58, and 0.065 (mg/g) for, MB, MV, RhB, and MO (eq S2). Interestingly, the adsorption efficiency of the material increased upon increasing the dye concentration from  $5 \times 10^{-5}$  M to  $10^{-4}$  M, and the calculated dye adsorption amount by ADES-4 for the individual dye MB, MV, RhB, and MO is 2.65, 3.09, 2.97, 1.19 mg/g. The adsorptive removal studies clearly demonstrate the prospects of both neutral MOFs toward obvious adsorption of cationic dyes over MO. Upon dye adsorption, the color of the off-white pristine MOF is changed as mentioned earlier, and the respective composite material is titled as ADES-4@dye (dye = MB, MV, RhB, or MO). The composite material thus obtained is further analyzed by different physicochemical analyses such as UVvis (solid state), FTIR, and PXRD techniques (Figure 2i and Figures S7–S8). FE-SEM and PXRD analysis of the pristine MOFs and ADES-4@dye was performed to investigate the morphological change and structural stability. MOF materials retain their structural and chemical integrity in ADES-4@dye composite as the experimental PXRD data showed an identical pattern with the pristine sample (Figure S8). FE-SEM images of original MOF materials revealed the microcrystalline nature, whereas ADES-4@dye composite adopts spherical morphology by the agglomeration of MOF with the respective dyes as depicted in Figure S9.

Zinc-based MOFs being nontoxic, a competitive adsorption study from a mixture of dyes was performed between the cationic and anionic dye mixture by ADES-4 bearing in mind that MO is least adsorbed (5%). To prepare the dye mixture, MO was mixed with the selected cationic dyes (MB, MV, and RhB) in an equimolar ratio (1:1; 10 mL) in each batch for the experiment. ADES-4 (100 mg) was added into aqueous solution of dye mixture and stirred continuously in dark conditions for 3 h. The selectivity of dye adsorption accomplished was assessed by UV–vis analysis from each batch of dye mixtures by monitoring the absorbance maxima of the corresponding dye MB (~664 nm), MV (~588 nm), RhB (~556 nm), and MO (~464 nm). As depicted in Figure 2j–l, the UV–vis spectra of dye mixture solutions showed



Figure 2. (a–h) UV–vis spectra of organic dyes (MB, MV, RhB, and MO) solution before (0 min) and after (180 min) adsorption study using ADES-4 and ADES-5; (i) solid state UV–vis spectra of ADES-4 and ADES-4@dye (dye = MB, MV, RhB and MO); (j–l) UV–vis spectra of organic dye mixture (MB + MO, MV + MO, and RhB + MO) solution before (0 min) and after (180 min) the adsorption study using ADES-4. (Inset digital images of visual color changes before (0 min) and after (180 min) dye adsorption experiments).



**Figure 3.** (a-d) UV-vis spectra of effluent from column chromatographic separation of individual dyes (MB, MV, RhB, and MO) using ADES-4 as the filler material; (e-g) UV-vis spectra of effluent from column chromatographic separation of dye mixtures (MB + MO, MV + MO, and RhB + MO) using ADES-4 as the filler material. (Inset digital images show the visual color change during the dye separation experiment using ADES-4 as a column chromatographic filler.)

noteworthy reduction in absorbance maxima for MB and MV but only a marginal decrease observed for RhB. This is also reflected as a visible color change of residual mixed dye solutions after 3 h, showing a light orange color demonstrating the major adsorption of MB and MV (Figure 2j-k) and only a

mild color change of the pink solution showing weak adsorption of RhB by ADES-4 (Figure 2l). The preferential adsorption of cationic dye from the mixed dye combination with MO is on order of MB > MV > RhB, and the spectroscopic and visual detection studies also supplement this



Figure 4. Schematic representation of a plausible dye adsorption mechanism via supramolecular interactions in ADES-4.

observation. Enthused by cationic dye adsorption results, we also applied ADES-4 as a stationary phase for the separation of individual and a mixture of dyes by a column chromatographic method from water. Experimental details/column preparation etc. are given in the supporting data, and a  $10^{-4}$  M concentration of respective dye solutions (MV, MB, RhB, and MO) was passed through the column of ADES-4. As displayed in Figure 3a–b, collected effluent of MB, and MV showed negligible color of the respective dye, indicating the complete removal of these dyes by the MOF filler. However, the residual eluent collected after passing through the column in the case of RhB and MO showed the color of the respective dyes, revealing low adsorption/no adsorption of these dyes by ADES-4 (Figure 3c–d).

Similarly, experiments were conducted for the separation of individual dyes from the dye mixture (MB + MO, MV + MO, and RhB + MO) by passing through the column of ADES-4. The orange color of the column eluent solution in all the mixed dye combinations clearly demonstrates the selective removal of positively charged dyes MV, MB, and RhB by the ADES-4 column leaving behind the anionic dye MO in residual solution (Figure 3e-g). These results further indicate the selective removal/separation of cationic dyes by ADES-4 from the mixture existing with anionic dye MO.

Selectivity of specific dye adsorption by MOFs can be influenced by many parameters.<sup>27,28</sup> Indeed, the presence of the acylamide group in L and -OH functionality of the **5OH-IP** can afford supramolecular interactions with the cationic dyes and the  $\pi \cdots \pi$  interactions between the aromatic moiety of the dye, and the ligand may probably be effective for the successful adsorptive removal of the cationic dye by ADES-4. The free hydroxyl group of **5OH-IP** and the acylamide group of L can facilitate donor/acceptor sites in hydrogen-bonding interactions with positively charged dyes by various supramolecular interactions on the surface, and the layered channels between the offset two-dimensional structures in ADES-4 can perhaps modify and act as a host toward cationic dyes for effective adsorption.

The free hydroxyl group and acylamide functionality in the linker of MOF can be comprehended as supramolecular interaction sites for the cationic dye molecules in the absorptive removal process on the surface as well as accommodation of guest dyes in between 2D layers of the ADES-4 host. Representative plausible noncovalent interactions between the guest MOF adsorbent and cationic dye MB are depicted in Figure 4. Thus, the hydroxyl group of 5OH-IP can allow O-H…N interactions with the lone pair of dimethyl amines, and the acylamide hydrogen of L can be involved in N-H...N interactions with the pyridyl nitrogen of MB supporting strong anchoring of the MB with the highest adsorption efficiency. The smallest size of MB among cationic dyes also favors the highest adsorption by ADES-4. The observed order of dye adsorption in the present investigation is MB > MV > RhB, which can also endorse the smallest size of MB, which can easily diffuse between the accessible 2D network layers compared to other cationic dyes and the mentioned probable three-point supramolecular interactions (Figure 4).

For practical applications, the desorption process is equally important, and the reversible adsorption property of MOFbased functional material plays a significant role in the containment of hazardous molecules including dyes that is important for sustainable development. Dye-releasing studies were conducted in methanol by soaking ADES-4@dye materials for 90 min. Progressive, time-dependent dye release into methanol is clearly visible by the naked eye not only by the increase in the color intensity but also reflected in the enhancement in the absorption band of the respective dyes in the UV-vis spectra. Digital photographs for representative progressive dye release in the case of MB with time and the steady enhancement in the absorbance maxima of MB (~652 nm) are shown in Figure S10a-b. Similarly, release experiments performed for the rest of the dyes also revealed that the colorless methanol solution steadily changes to a respective dye color and enhancement of the respective absorption band in the UV-vis spectroscopy representing time-dependent gradual release of the dyes (Figure S10c-f). A recyclability experiment of ADES-4 was conducted up to four adsorptiondesorption cycles for MB, and the PXRD pattern of the recovered material confirmed the stability of framework during the removal process (Figures S11-S12). Similarly, PXRD patterns for ADES-4 recovered after dye-releasing experiments in methanol matched well with pristine material confirming the chemical stability of the MOF skeleton (Figure S12).

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Scheme 2. Dehydration Reaction of Fructose/Glucose to 5-Hydroxymethylfurfural (HMF) Conversion



#### Table 1. Optimization of Reaction Conditions for Dehydration Reaction of Monosaccharides Fructose/Glucose in to 5-Hydroxymethylfurfural (HMF)

entry	substrate	catalyst (mmol)	solvent	temp (°C)	time (min)	HMF yield (%) <sup>a</sup>
1	fructose	blank	DMSO	120	60	8.50
2	fructose	ADES-4 (0.02)	DMSO	120	60	22.35
3	fructose	ADES-4 (0.05)	DMSO	120	60	42.47
4	fructose	ADES-4 (0.1)	DMSO	120	60	75.01
5	fructose	ADES-4 (0.15)	DMSO	120	60	72.72
6	fructose	ADES-4 (0.2)	DMSO	120	60	71.83
7	fructose	ADES-4 (0.1)	DMSO	60	60	26.90
8	fructose	ADES-4 (0.1)	DMSO	80	60	41.36
9	fructose	ADES-4 (0.1)	DMSO	100	60	53.26
10	fructose	ADES-4 (0.1)	DMSO	140	60	75.59
11	fructose	ADES-4 (0.1)	DMSO	120	30	57.99
12	fructose	ADES-4 (0.1)	DMSO	120	90	75.19
13	fructose	ADES-4 (0.1)	DMSO	120	120	75.45
14	fructose	ADES-4 (0.1)	THF	reflux	60	12.30
15	fructose	ADES-4 (0.1)	water	reflux	60	1.43
16	fructose	ADES-4 (0.1)	EtOH	reflux	60	7.11
17	fructose	ADES-5 (0.1)	DMSO	120	60	73.86
18	fructose	<b>50H-</b> H <sub>2</sub> <b>IP</b> (0.1)	DMSO	120	60	22.88
19	fructose	L (0.1)	DMSO	120	60	17.21
20	fructose	$Zn(NO_3) \cdot 6H_2O(0.1)$	DMSO	120	60	23.46
21	fructose	$Cd(NO_3) \cdot 4H_2O(0.1)$	DMSO	120	60	20.52
22	glucose	ADES-4 (0.1)	DMSO	120	60	58.88
<sup>a</sup> Product (HI	MF) yield determi	ned by HPLC analysis.				

Catalytic Performance of MOF in the Transformation of Fructose/Glucose to 5-Hydroxymethylfurfural (HMF). Several recent reports on 5-substituted isophthalate as linkers in MOFs support the capability of these materials for catalysis and other applications.<sup>59,60</sup> Phenolic -OH groups of 5hydroxyisophthalic acid are well documented for their hydrogen-bonding ability with guest molecules.<sup>61</sup> Interestingly, reports on solid acid catalysts highlighting the catalytic efficiency of phenolic -OH groups along with other functional groups for the production of HMF are also available in the literature.<sup>62–64</sup> Catalytic conversion of fructose to HMF by MOF-based materials has been scantly explored, and as far as we know this is the one of the primary report on MOF as a heterogeneous catalyst decorated with hydroxyl/acylamide functional groups for the dehydration of C6 sugars to HMF. High thermal and chemical stability and the presence of uncoordinated hydroxyl groups as potential interaction sites for catalysis in both MOFs motivated us to find their applications in catalysis. Hence, we decided to exploit the catalytic efficiency of synthesized MOFs for the dehydration of fructose/glucose to HMF (Scheme 2).

The performance of ADES-4 as a heterogeneous catalyst was evaluated in the presence of 10 mg of fructose as a substrate in the reaction medium of DMSO (1 mL), and the observed

results are summarized in Table 1. Initially, a blank experiment at 120 °C for 60 min ended with a poor yield of HMF, accentuating the need for a suitable dehydrating catalyst for the conversion (Table 1, entry 1). The influence of ADES-4 loading on the dehydration reaction was checked by utilizing a variable catalyst amount (Table 1, entry 2-6). In the beginning, 0.02 mmol of ADES-4 noticeably increased the HMF yield compared to the blank reaction (Table 1, entry 2), indicating the catalytic effectiveness of the material for fructose dehydration. The synergistic effect of weakly acidic -OH groups and acylamide groups of the functionalized N-donor ligand present in ADES-4 may have some influence in the dehydration process. The HMF yield of 42.47% was observed with a loading of 0.05 mmol of catalyst (Table 1, entry 3). A further increase in catalyst loading to 0.1 mmol resulted in an HMF yield of 75.01% (Table 1, entry 4). A negligible decrease was observed in the HMF yield with 0.15 and 0.2 mmol of catalyst, which may be due to the transformation of HMF to other byproducts such as levulinic and humic acid. The effect of temperature on the dehydration reaction was optimized by utilizing 0.1 mmol of ADES-4 catalyst under varying reaction temperatures (Table 1, entries 7-10). When the reaction temperature was dropped to 60 °C, only a 26.90% HMF yield was obtained after 60 min (Table 1, entry 7). The increase in

temperature from 60 to 80 °C showed a steady increase in yields up to 41.36% HMF in the same reaction time. A further rise in temperature to 100 °C disclosed a concurrent surge in the HMF yield (Table 1, entry 8). However, an almost comparable HMF yield was obtained at 120 and 140 °C with a similar reaction time of 60 min (Table 1, entries 4 and 10). Further, the effect of reaction time on dehydration of fructose was optimized by running a reaction in the presence of 0.1 mmol of ADES-4 at 120 °C by varying the reaction time 30, 90, and 120 min (Table 1, entries 11-13). A decrease in the HMF yield was observed with a reduced reaction time of 30 min (Table 1, entry 11), but an increase in product yield with a negligible difference was noticed with an extended reaction time of 90 and 120 min (Table 1, entries 12-13). It was evident from the literature that DMSO plays an important role in a dehydration reaction.<sup>65–68</sup>

The effect of other solvents on dehydration was also tested by conducting similar reactions in the presence of THF, water, and ethanol as solvents under reflux conditions (Table 1, entries 14-16). All the reactions ended with poor HMF yield within the stipulated reaction time. A systematic study of various parameters indicates 0.1 mmol of ADES-4 at 120 °C for 60 min as the ideal optimized conditions to achieve 75.01% HMF yield. The catalytic efficiency of ADES-5 was also checked by replacing ADES-4 in the model reaction under similar optimized reaction conditions (Table 1, entry 17). Commensurate HMF yield advocates the catalytic efficiency of ADES-5 in a dehydration reaction. The catalytic effect of building blocks of both ADES-4 and ADES-5 was also tested by utilizing 0.1 mmol of the individual component as a catalyst in the model reaction (Table 1, entry 18-21). However, poor HMF yield in all four reactions supports the efficacy of ADES-4 and ADES-5 material for fructose dehydration. To check the substrate scope, the model reaction under optimum reaction conditions was also tested for glucose (Table 1, entry 22). The decrease in HMF yield (58.88%) observed in the case of glucose dehydration may be attributed to the additional step involved in the conversion of glucose to fructose before the dehydration process. Product identification and the catalytic yield were determined by NMR spectroscopy and HPLC analysis, respectively (Figure S13-S16). Comparison of reported MOF-based catalysts toward the catalytic conversion of HMF with the present investigation is provided in the Supporting Information (Table S4). Albeit MOF catalysts bearing metals such as Cr, Sn, and Hf and MOFs with -SO<sub>3</sub>H/-COOH groups and with guest functional molecules showed a higher yield in fructose to HMF conversion, the glucose to HMF yield and efficiency are better/on par by ADES-4 than the reported ones with sensible reaction conditions (Table S4). Probably, ADES-4 with functionally decorated hydroxyl and acylamide groups may synergistically be involved in the twostep process involving glucose to fructose conversion followed by dehydration favoring efficient product yield of HMF. It is well documented in the literature that the mechanism involving glucose to HMF conversion proceeds via isomerization followed by dehydration.  $^{36,69-72}$  In the first catalytic cycle, fructofuranose was generated via a 1,2-hydride transfer, followed by cyclization from  $\alpha$ -glucopyranose. The probable mechanism in the present investigation also follows the same pathway in which synergistic effect engendered through the surface, the layered channels, and the availability of Brønsted acid sites on functionalized linkers in both MOFs plays an important role in the conversion of glucose/fructose to HMF.

Recyclability of the catalyst is important for real-world practical applications, and no considerable decrease in product yield was observed by the ADES-4 catalyst for up to six cycles, revealing its good recyclability (Figure S17). The recovered catalyst after the final catalytic cycle by filtration, washing, and drying showed identical matching of PXRD and FTIR data with assynthesized catalysts revealing the stability/integrity of the framework (Figures S18–S19).

#### CONCLUSIONS

Two isostructural mixed-ligand 2D MOFs with Zn(II)/Cd(II) metal centers and functionally decorated dicarboxylate/Ndonor ligands possessing high thermal/chemical stability were successfully constructed by a versatile synthetic approach such as diffusion/conventional reflux/mechanochemical methods and analyzed by different physicochemical techniques. Both these materials show selective removal of cationic dyes (MV and MB) not only as independently but also from a mixture of anionic dye MO. The separation studies on a mixture of dyes (MO with cationic dyes) shows efficient removal of MB/MV from the mixture, which is also demonstrated using ADES-4 as a column filler. A probable adsorption mechanism is proposed on the basis of SXRD data in which the MOFs can act as an active site favoring the adsorption process on its surface most likely by lodging the guest dyes between the 2D layers of host networks with various supramolecular interactions. Both MOFs turned out to be promising adsorbent materials for reversible dye removal with specificity. In addition to the application of ADES-4 for the reversible removal of cationic dyes, both MOFs also act as heterogeneous catalysts for the transformation of C6 monosaccharides to yield 5-hydroxymethylfurfural (HMF), an industrially important, high-value chemical intermediate. Overall, the present studies highlight the synthesis of bifunctional MOFs as reversible adsorbents for selective adsorption/separation of noxious cationic dyes and as catalysts for transformation of fructose and glucose into the value-added chemical intermediate HMF.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01208.

Experimental, crystallography, FTIR, TGA, PXRD, UVvis, NMR spectra (PDF)

#### **Accession Codes**

CCDC 2067806–2067807 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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# Inorganic Chemistry

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Notes

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