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Stoichiometry-Regulated Synthesis of Three Adenine-Based Coordination Polymers for Catalytic Excellence through the Synergistic Amalgamation of Coordinative Unsaturation and Lewis Basic Sites

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AbSTRACT: Nucleobase adenne is a promising candidate for synthesizing fascinating coordination polymers (CPs) due to the presence of five potential metal-ion binding centers. In recent years, CPs have emerged as promising Lewis acid-base centers containing heterogeneous catalysts for a wide range of organic transformations. However, the crucial role of stoichiometric regulations of the starting materials and their consequential impact on catalytic performance are rarely studied. Herein, we have synthesized three adenine (Ad)-based cadmium CPs with 5-nitro isophthalic acid (H₂NIPA) by a mixed linker approach by tuning the substrate's stoichiometric proportion. The single-crystal X-ray diffraction analysis of the synthesized CPs, SSICG-11, $[Cd(Ad)(NIPA)(H_2O)]$ ·H₂O; SSICG-12, $[Cd(Ad)_2(NIPA)(H_2O)]$; and SSICG-13, $[Cd_4(Ad)(NIPA)_3]$ ·H₂O·DMF, reveals that these three compounds exhibit distinct asymmetric units, each reflecting varying precursor proportions. Due to their high chemical stability and the presence of both Lewis acidic–basic sites, SSICG-11–13 were employed



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as heterogeneous catalysts for Hantzsch and Strecker reactions. However, SSICG-12 is more efficient due to its capacity to form an open metal sites (OMSs) and the presence of a higher number of adenine moieties. Overall, this study demonstrated the stoichiometrically controlled synthesis of adenine-based CPs and dissected their efficiency as a heterogeneous catalyst by correlating their structures and compositions.

INTRODUCTION

The infinite networks formed by the interconnection of metal ions and organic ligands are defined as coordination polymers (CPs), which can form 1D, 2D, or 3D structures.^{1,2} On the other hand, metal-organic frameworks (MOFs) are subgroups of CPs, which are robust crystalline porous materials formed by the coordination interaction between the organic ligands and inorganic units, like metal ions or metal clusters.^{3,4} CPs and their derivatives have recently emerged as one of the fastestgrowing materials due to their rigid structure, high surface area, and tunability, and they show diverse applications in the areas of gas storage and separation, catalysis, proton conduction, drug delivery, adsorption, sensing, etc.⁵⁻¹⁰ The synthetic strategy of CPs involves solvothermal, hydrothermal, diffusional, microwave-assisted, and mechanochemical procedures.^{11,12} Additionally, using techniques such as linker exchange, postsynthetic modification, and functional group grafting, CPs can be specially designed to have suitable characteristics and applications by tuning the organic linkers and inorganic nodes.^{13–15} Hence, the judicious selection of metal ions and organic linkers is crucial for the synthesis of CPs. A diverse array of organic linkers containing alkyl (-R), thiol (-SH), amines $(-NH_2)$, alcohol

(–OH), etc. enhance the diversity of their structures for targeted applications. $^{\rm 16-19}$

Biologically active ligands, such as adenine, are a unique building block for synthesizing CPs because they contain many binding sites to coordinate with metal ions or nodes.²⁰ The rigid structure of adenine fused two heterocyclic moieties, imidazole and pyrimidine, and one amine group, which boasts five possible binding sites (Figure 1).²¹ The different binding modes have been utilized over the years to synthesize fascinating CPs by tuning metal ions, reaction conditions, solvent, composition, and pH.^{22–25}

In recent years, CPs have emerged as excellent heterogeneous catalysts due to the possibility of both Lewis acidic metal centers and Lewis basic nitrogenous organic linkers.^{26–28} However, the significance of stoichiometric regulations of the starting materials and their consequential impact on catalytic perform-

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Figure 1. Structure of adenine with binding sites.

ance is rarely studied because the synthesis of the pure phase of bulk materials can be quite challenging.^{29,30} Cd-CPs, in particular, exhibit Lewis acidity due to the ability of cadmium ions to accept electron pairs from Lewis bases; for this reason, many Cd-CPs have been utilized as heterogeneous catalysts for a diverse array of organic transformations.^{31–36} The Hantzsch and Strecker reaction is significant in synthetic organic chemistry as these reactions provide a route to synthesizing compounds of biological and pharmaceutical importance.^{37,38} Hantzsch reactions synthesize pyridines and dihydropyridines, while Strecker reactions offer a straightforward route to α -amino nitriles, which can be hydrolyzed into amino acids.^{39,40} Previously, the reactions relied on homogeneous catalysis, which creates a problem in the catalyst separation stage and can be addressed by using CPs as heterogeneous catalysts, simplifying the separation processes and promoting recyclability, thus promoting a greener approach.^{41,42}

Herein, we have synthesized three adenine (Ad)-based cadmium CPs with 5-nitro isophthalic acid (H₂NIPA) by a mixed linker approach. In this synthetic approach, we have highlighted the critical role of controlling the stoichiometric proportion of the substrate on CP fabrication. The structural analysis of the synthesized CPs, SSICG-11, [Cd(Ad)(NIPA)- (H_2O)]· H_2O ; SSICG-12, $[Cd(Ad)_2(NIPA)(H_2O)]$; and SSICG-13, $[Cd_4(Ad)(NIPA)_3] \cdot H_2O \cdot DMF$, was performed by SCXRD analysis, and interestingly, these three CPs contain distinct asymmetric units in their unit cell which plays a critical role in their properties. The stability and properties of the synthesized CPs were further analyzed using analytical techniques like PXRD, infrared spectroscopy (IR), Brunauer-Emmett-Teller (BET) analysis, field emission scanning electron microscopy (FE-SEM), and thermogravimetric analysis (TGA). The presence of Lewis acidic and Lewis basic sites in SSICG-11-13 motivated us to explore their potential as a catalyst for Hantzsch and Strecker reactions. Interestingly, SSICG-12 shows significantly higher efficiency than SSICG-11 and 13, indicating the significance of stoichiometric manipulation in CP's structures and efficiency. Finally, the structural and property relationship of SSICG-11-13 was analyzed, and rational mechanisms were proposed based on correlating our results and recent reports. Although CPs have been utilized as a



Figure 2. Synthesis of three adenine-based CPs (SSICG-11-13).



Figure 3. (a) 1D structure of SSICG-11, (b) asymmetric unit of SSICG-11, (c) 1D structure of SSICG-12, (d) asymmetric unit of SSICG-12, (e) 2D structure of SSICG-13, and (f) asymmetric unit of SSICG-13.



Figure 4. Structural description of SSICG-12. (a) Ball-and-stick model of SSICG-12, (b) coordination of metal centers, (c) coordination mode of adenine, and (d) coordination mode of NIPA.

heterogeneous catalyst for a wide range of organic transformations over the years, attention has recently been shifted to the synthesis of drugs or natural products.^{34,43} The emerging focus holds significant potential for advancing the sustainability of pharmaceutical industries. In this work, we have utilized our most efficient catalyst, SSICG-12, to synthesize a calcium channel blocker, nemadipine B, which is a 1,4-dihydropyridine (1,4-DHP)-based drug, by the Hantzsch reaction and an α aminonitrile-based natural product, girgensohnine, via the Strecker reaction.

EXPERIMENTAL SECTION

Materials and Characterizations. The details regarding the materials used and the physical measurements conducted, including



Figure 5. Simplified pictorial representations of (a) SSICG-11, (b) SSICG-12, and (c) SSICG-13.

single-crystal X-ray diffraction (SCXRD), powder X-ray diffraction (PXRD), Fourier-transform infrared (FT-IR) spectroscopy, BET surface area analysis, TGA, and FE-SEM along with the specific software utilized in these analyses, are provided in the Supporting Information section.

RESULTS AND DISCUSSION

Synthesis of Adenine-Based CPs (SSICG-11–13). Cadmium(II) nitrate tetrahydrate (Cd(NO₃)₂·4H₂O) (0.2 mmol), 5-nitro isophthalic acid (H₂NIPA) 0.2 mmol, and adenine (0.2 mmol for SSICG-11 and 0.4 mmol for SSICG-12) were taken in a 15 mL glass vial, and 4 mL of a solvent mixture of DMF/H₂O (1:3) and 20 μ L of HNO₃ were added to it and sonicated for 10–15 min. Then, the glass vial was kept at 100 °C in a preheated oven for 24 h, forming colorless crystals. The identical conditions were applied to SSICG-13, differing only in the substrate's molar ratio, consisting of 0.4 mmol of Cd(NO₃)₂. 4H₂O, 0.3 mmol of H₂NIPA, and 0.1 mmol of adenine (Figure 2). Finally, the crystals were collected by filtration, washed with water, and air-dried.

Structural Analysis. The structural information on all the compounds is provided in Table S1. CCDC: 2360322–2360324 contain the crystallographic data of these compounds.



Figure 6. (a-c) PXRD of calculated and as-synthesized SSICG-11-13. (d) VT-PXRD of SSICG-12. (e) FT-IR spectra of SSICG-11-13. (f) TGA of SSICG-11-13. FE-SEM pictures of (g) SSICG-11, (h) SSICG-12, and (i) SSICG-13. (j-m) Elemental mapping of SSICG-12.

SSICG-11. SSICG-11 (Figures 3a and S1a) crystallizes in the triclinic crystal system with space group $P\overline{1}(2)$. The asymmetric unit of SSICG-11 comprises one NIPA, one adenine, and one cadmium alongside one coordinated and one lattice water molecule (Figure 3b). The metal center, Cd, adopts the distorted pentagonal bipyramidal structure (Figure S1b). The cadmium metal center coordinates with six oxygen and one nitrogen. Nitrogen comes from the pyrimidine moiety of adenine (Figure S1c), and five oxygens come from two NIPA linkers (Figure S1d). The two carboxylic acid groups of the ligand NIPA bind with the three metal ions, and the coordination motif of the two carboxylic acid groups of one NIPA is different (Figure S1e). One coordinates with only one cadmium, whereas the other one coordinates with two cadmiums ($\mu_3 - \eta^2 \eta : {}^1 \eta^1 \eta^1$ mode of coordination). Interestingly, the carboxylic oxygen of NIPA coordinates with two cadmiums via the Cd(II)-(μ -O) bond and forms a 1D ladder structure (Figure S1f). Selected bond distances and angles are shown in Table S6a-c.

SSICG-12. SSICG-12 (Figures 3c and 4a) crystallizes in the triclinic crystal system with space group $P\overline{1}(2)$. The asymmetric unit of SSICG-12 contains one NIPA, two adenines, and one cadmium alongside one coordinated water molecule (Figure 3d). The metal center Cd in SSICG-12 is coordinated with four oxygen (three from NIPA and one from water) and two nitrogen atoms (from two adenine), forming a distorted octahedral environment (Figure 4b). The adenine ligand is connected to the metal center Cd through one imidazole nitrogen atom, and amine groups remain free (Figure 4c). The acid ligand NIPA is coordinated to Cd through the oxygen of the carboxylic acid groups; on one side, two oxygen atoms of the carboxylic acid group are connected, and on the other side, one oxygen atom of the carboxylic acid group is connected to the metal center (μ_2 - $\eta^1 \eta^{11} \eta^1 \eta^0$ mode of coordination) (Figure 4d). The crystal structure also reveals the formula of SSICG-12, which is $[Cd(Ad)_2(NIPA)(H_2O)]$. Overall, a 1D chain structure is formed. The selected bond distances and angles are shown in Table S7a-c.



Figure 7. (a) N_2 adsorption isotherm for SSICG-11-13 at 77 K. (b) CO_2 adsorption-desorption isotherm of SSICG-11-13 at 298 K. (c) Surface area and (d) CO_2 adsorption capacity comparison between SSICG-11-13.

SSICG-13. SSICG-13 (Figures 3e and S2a) crystallizes in the triclinic crystal system with space group $P\overline{1}$ (2). The asymmetric unit of SSICG-13 contains four crystallographically different Cd(II), three nitro-isophthalates, one adenine, two lattice solvent molecules, a DMF, and a water molecule (Figure 3f). In the structure, two 1D chains are formed by Cd, NIPA, and adenine (Figure S2b), which are connected by NIPA (Figure S2c), and finally, a 2D layer structure is formed. The coordination environment of the different cadmium is shown in Figure S2d, where Cd1 has a distorted pentagonal bipyramidal geometry, whereas Cd2, Cd3, and Cd4 adopt distorted octahedral geometry. The distorted pentagonal bipyramidal geometry of Cd1 originates from five oxygens of the carboxylic acid moiety and one nitrogen (N1) from the imidazole moiety of adenine. The octahedral geometry of Cd2 originates from three pairs of oxygen: O2, O7, and O10. Meanwhile, octahedral Cd3 is connected with three pairs of oxygen: O13, O16, and O3, whereas Cd4 is connected with five oxygen and one nitrogen (N4) atoms from the pyrimidine moiety of adenine and acquires distorted octahedral geometry. In this structure, unlike SSICG-11,12, two nitrogens of adenine (one each from imidazole and pyrimidine moieties of adenine) are connected to the cadmium metal center Cd1 and Cd4 (Figure S2e). The acid ligand NIPA shows three different types of bonding patterns μ_{5} - $\eta^{1}\eta^{1}$: $\eta^{1}\eta^{0}$, μ_{5} - $\eta^{1}\eta^{1}$: $\eta^{1}\eta^{0}$, and μ_{4} - $\eta^{1}\eta^{1}$: $\eta^{1}\eta^{0}$ (Figure S2f). The selected bond distances and angles are shown in Table S8a-c. In the framework of SSICG-13, the benzene rings of NIPA are positioned by a distance of 3.73, 3.83, and 3.48 Å from each other (Figure S2g,h). A DFT analysis reveals that the benzene rings, separated by 3.48 Å, are engaged in $\pi \cdots \pi$ stacking interactions with a calculated $\pi \cdots \pi$ stacking stabilization energy of around 0.71 kcal/mol.⁴⁴

Structural Comparison of SSICG-11–13. Basically, the different composition of starting materials leads to three structurally different CPs SSICG-11–13. SSICG-11 forms a 1D ladder structure where oxygen coordinates with two

cadmiums via the Cd (II)-(μ -O) bond (Figure 5a), whereas SSICG-12 forms a 1D chain structure (Figure 5b). SSICG-11 and SSICG-12 contain one coordinated water molecule in their asymmetric unit, but SSICG-11 contains one adenine unit, whereas SSICG-12 contains two adenine units. In the case of SSICG-13, it forms a 2D layer-type structure where one adenine moiety is connected to two crystallographically different cadmiums, and there is no coordinated water molecule in the asymmetric unit (Figure 5c).

Physical Characterizations. Synthesis of bulk amounts of molar ratio-controlled CPs can be challenging due to difficulties associated with precisely maintaining accurate molar ratios.^{45,46} However, we successfully synthesized the bulk scales of SSICG-11–13 by doubling the reactant ratio in optimized conditions. The phase purity of these bulk samples was confirmed by PXRD, which perfectly matches the calculated PXRD of SSICG-11-13, respectively (Figure 6a-c). In VT-PXRD, the PXRD patterns of SSICG-11 and 12 were recorded from room temperature (rt) to 140 °C. The peak at $2\theta = 15.76^{\circ}$ for SSICG-11 (Figure S3a) and $2\theta = 11.36^{\circ}$ for SSICG-12 (Figure 6d) shows a gradual leftward shift and reverts to its original position upon cooling, confirming the reversible removal of the coordinated water molecule of these CPs.⁴⁷ The chemical stability of all three synthesized CPs was also tested by PXRD, where SSICG-11-13 were immersed in different organic solvents and aqueous solutions of different pH 3-10 for 24 h. Subsequently, PXRD was performed, which showed no significant loss of crystallinity and confirmed the high chemical stability of the compounds (Figure S3b-d). The presence of coordinated water is also indicated by FT-IR spectra of SSICG-11 and 12 by the presence of a peak around 3570 cm^{-1} , which is absent in SSICG-13 (Figure 6e).⁴⁸ The thermal stability of SSICG-11-13 was examined by TGA at room temperature to 800 °C under N₂ (Figure 6f). The initial weight loss of SSICG-11 and SSICG-12 compounds is 7.4% (calcd 7.3%) and 3.7% (calcd 3%), respectively, due to the loss of water molecules from around 150 to 190 °C. In the case of SSICG-13,



Figure 8. Catalytic utilization of SSICG-11–13 in Hantzsch and Strecker reactions.



Figure 9. Catalytic utilization of SSICG-11-13 in the Hantzsch condensation reaction.

Table 1. Optimization of	f Reaction	Conditions f	for Hantzsch	ı Cond	lensation
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entry	catalyst	solvent	temperature (°C)	time (h)	NMR yield* (conversion) (%)	isolated yield (%)
1	SSICG-12		60	4	17	16
2	SSICG-12	CH_2Cl_2	60	4	22	20
3	SSICG-12	CHCl ₃	60	4	31	28
4	SSICG-12	CH ₃ CN	60	4	40	40
5	SSICG-12	CH ₃ OH	60	4	72	70
6	SSICG-12	C ₂ H ₅ OH	60	4	100	96
7	SSICG-11	C ₂ H ₅ OH	60	4	90	85
8	SSICG-13	C_2H_5OH	60	4	61	58
9	$Cd (NO_3)_2 \cdot 4H_2O$	C_2H_5OH	60	4	28	26
10	Cd $(NO_3)_2$ ·4H ₂ O + adenine + H ₂ NIPA	C ₂ H ₅ OH	60	4	31	29
11	adenine	C_2H_5OH	60	4	-	-
12	H ₂ NIPA	C_2H_5OH	60	4	-	-

"Reaction condition: benzaldehyde (1 mmol), ethyl acetoacetate (2 mmol), ammonium acetate (1 mmol), solvent (1 mL), and catalyst (2 mol %). *The yields are calculated based on ¹H NMR of the crude.

the initial water loss of 7.9% (calcd 7.7%) in the range of 188 to 240 °C is due to the loss of water and DMF molecules. All three compounds show high chemical stability, more than 300 °C. FE-SEM analysis revealed the block shape morphology of all three CPs (Figure 6g–i), and the energy-dispersive X-ray elemental mapping confirmed the uniform distribution of the constituent elements (Figures 6j–m and S4a,b).

Gas Adsorption Analysis. To calculate the surface area of SSICG-11-13, N₂ adsorption experiments were performed at 77 K. The samples were prepared for this experiment by immersing the compounds in methanol for 12 h, followed by three cycles of methanol replacement. Then, the samples were vacuum oven-dried at 60 °C, which made them solvent-free. The measured BET surface area of SSICG 11-13 is 12.76, 13.31, and 24.30 m²/g (Figure 7a,c), respectively. The low surface area of the synthesized CPs aligns with the solvent-accessible voids calculated from their crystal structures using PLATON.⁴⁹ The framework of SSICG-11, SSICG-12, and SSICG-13 contains 1.12% (12 Å 3 of 801.51 Å $^3),$ 0.80% (9 Å 3 of 1121.59 Å $^3),$ and 9.69% (190 Å³ of 1959.15 Å³) solvent-accessible voids, respectively. Interestingly, SSICG-12 has a lower surface area than SSICG-13 and a comparable surface area with SSICG-11, but it shows a multifold higher CO_2 adsorption capacity (9.56

cm³ g⁻¹) than SSICG-11 (1.32 cm³ g⁻¹) and SSICG-13 (1.31 cm³ g⁻¹) (Figure 7b,d). The higher CO₂ adsorption capacity of SSICG-12 is most likely because of the higher density of the Lewis basic nitrogen-containing adenine moiety, which causes strong interaction with CO₂ and exhibits hysteresis in the CO₂ isotherm. ^{50,51}

Catalytic Utilization of SSICG-11–13 in Lewis Acid– Basic Catalytic Reactions. The presence of Lewis acidic Cd²⁺ and Lewis basic centers (nitrogen center in adenine) encouraged us to examine the catalytic activity of the synthesized CPs (SSICG-11–13) as a bifunctional heterogeneous catalyst.^{34,52,53} Here, we have explored the comparative efficiency of the three different adenine-based CPs and analyzed the role of precision engineering for catalytic excellence (Figure 8).

Catalytic Hantzsch Condensation Reaction. The Hantzsch condensation, named after Arthur Hantzsch, is a powerful organic reaction used to synthesize many heterocyclic compounds, particularly substituted pyridine derivatives. We have examined our synthesized CPs, SSICG-11–13, as a catalyst for the Hantzsch condensation reaction by taking benzaldehyde (1 mmol) as a model substrate and reacting it with a mixture of ethyl acetoacetate (2 mmol) and ammonium acetate (1 mmol)



Figure 10. Optimization of the Hantzsch condensation reaction by the catalyst SSICG-12, with respect to (a) temperature, (b) time (kinetic study), (c) amount of catalyst (mol %), and (d) hot filtration leaching test (all the yields are calculated from ${}^{1}H$ NMR).

to synthesize 1,4-DHPs (Figure 9). The solvent, temperature, and amount of the catalyst were varied to optimize the reaction. Initial reaction screening was done in solvent-free conditions, which gave a lower yield (Table 1, entry 1). Subsequently, the reactions were evaluated across a spectrum of solvents, including chloroform, dichloromethane, acetonitrile, methanol, and ethanol (Table 1, entries 2-6). The results indicate the significance of polar solvents, where ethanol acts as the most suitable solvent.

After solvent optimization, the reaction temperature was optimized, and the reaction NMR yield was 45% (42% isolated yield) at rt (30 °C) and a maximum NMR yield of 100% (96% isolated yield) was obtained at 60 °C (Figure 10a) (Figure S9a,b). The catalyst amount was gradually increased from 1 to 2 mol % for the reaction to identify the exact catalyst requirement. The result demonstrated that the catalyst exhibited a maximum yield when 2 mol % of the catalyst was used (Table 1, entry 6) (Figures 10c and S5). Similarly, the reaction time was optimized, and the reaction gave a maximum yield in 4 h when 2 mol % of SSICG-12 was used in an ethanol solvent (Figure 10b). In this optimized condition, SSICG-11 gives a 90% NMR yield (85% isolated yield); this may be due to the presence of only one Lewis basic adenine moiety in the structure of the catalyst (Table 1, entry 7).⁵⁴ Interestingly, SSICG-13, a 2D CP, shows a significantly lower efficiency (NMR yield 61%; 58% isolated yield) than SSICG-11 and 12 in optimized reaction conditions (Table 1, entry 8) (Figure S6). The low efficiency of SSICG-13

can be explained by the absence of coordinated water in the structure of the crystal, which is unable to generate an unsaturated metal center by activation.^{47,55} Controlled experiments were performed with precursor materials (e.g., Cd- $(NO_3)_2$ ·4H₂O, adenine, H₂NIPA, and a combination of Cd(NO₃)₂·4H₂O, adenine, and H₂NIPA) which resulted in low yields (<32%). This outcome nullifies the major role of precursor materials in catalysis (Table 1, entries 9–12) and establishes the importance of the synthesized catalysts. It is worth mentioning that SSICG-12 shows better-to-comparable efficiency with some of the previously reported catalysts (Table S2).

Catalyst Recyclability and Substrate Scope. A key characteristic of heterogeneous catalysts is their recyclability.⁵⁶ In this case, the recyclability of the catalyst was tested up to eight cycles. After each cycle, the catalyst was collected via centrifugation, washed with methanol, and dried in a vacuum oven. Comparatively, SSICG-12 did not show any significant downgrade in efficiency (Figure S7a). PXRD was performed after each cycle, and no significant loss in crystallinity was observed (Figure S7b), endorsing SSICG-12 as a stand-out heterogeneous catalyst. Also, the FE-SEM image of the recycled catalyst reveals that its block-shaped morphology remains intact, establishing SSICG-12 as an ideal heterogeneous catalyst (Figure S8).⁵⁷

A hot filtration test was performed to examine any possible chance of leaching of the catalyst. After 1 h, the catalyst was



Figure 11. (a–i) Substrate scopes: aldehydes (1 mmol), ethyl acetoacetate (2 mmol), ammonium acetate (1 mmol), solvent (1 mL), 2 mol % of SSICG-12 as the catalyst. *The yield of the model substrate (benzaldehyde) is calculated as 100% based on 1 H NMR and 96% as isolated yield. The yields of the substrate scopes are isolated yields calculated based on aldehyde.



Figure 12. Proposed mechanism of the Hantzsch condensation reaction.

separated from the reaction mixture, allowing the reaction to proceed for an additional 3 h, where no further improvement in product yield was observed, indicating the catalyst's nonleaching behavior (Figure 10d). To further confirm this, the filtrate of the reaction mixture was analyzed by ICP–MS, which revealed a negligible presence of Cd^{2+} (0.480 ppb) and ruled out the indication of leaching during this reaction.

Substrate Variation in Hantzsch Condensation. After optimizing the model reaction and being inspired by the excellent efficiency of SSICG-12, the catalyst's capacity was examined on a wide spectrum of aldehyde substrates containing

electron-donating and -withdrawing groups and characterized by ¹H NMR (Figures S9a–i). It was observed that the substratecontaining the electron-withdrawing group gives a relatively higher yield than the electron-donating-group-containing substrate (Figure 11a–i). This may be due to the ratedetermining step of the reaction, which is a nucleophilic addition reaction and stabilizes more by an electron-withdrawing group.³⁴ The substrate 9-anthracene carboxaldehyde gives a very low yield; this may be due to the electron-rich nature, bulkier structure, and limited accessibility to surfaceactive sites, which restricts its activation by the catalyst.⁵⁸



Figure 13. Synthesis of nemadipine B. Reaction condition: 2,3-dichlorobenzaldehyde (1 mmol), ethyl acetoacetate (2 mmol), ammonium acetate (1 mmol), solvent (1 mL), catalyst (2 mol %), 4 h, 60 °C; TON = 48; TOF = 12 h⁻¹.



Figure 14. (a-g) Reaction conditions: aldehyde substrates (1 mmol), aniline (1 mmol), TMSCN (1.1 mmol), SSICG-12 (1 mol%). *The yield of the model substrate (benzaldehyde) is calculated as 100% based on ¹H NMR and 97% as isolated yield. The yields of the substrate scopes are isolated yields calculated based on aldehyde. TOFs (h^{-1}) are the same as TONs.

Mechanism of the Hantzsch Condensation Reaction. After a thorough literature survey and based on experimental observations, a plausible mechanism for the SSICG-12-catalyzed Hantzsch condensation (Figure 12) is proposed. 34,41,54,59,60 As previously discussed, the model reaction was performed with the precursor materials which gave lower yields, underscoring the importance of the synthesized CPs in the reaction. Since the synthesized CPs are not highly porous, the catalytic reaction predominantly takes place on their surface.⁶¹ The proposed mechanism for Hantzsch condensation catalyzed by CPs containing Lewis acidic (Cd center) and basic sites (N sites of adenine) involves the following steps: (i) activation of substrates: the Lewis acidic sites (especially OMS) of the CPs interact with the substrates aldehyde and β -ketoester, which accept electron density from the carbonyl groups and reduce the C=O bond strength which enhances their susceptibility to nucleophilic attack. Simultaneously, the Lewis basic sites of the catalyst also activate ethyl acetoacetate by accepting its proton. (ii) Nucleophilic addition and formation of enamine: ammonia formed by ammonium acetate reacts with activated carbon of the β -ketoester, forming the imine intermediate that undergoes tautomerizations to form an enamine. (iii) Addition reaction of aldehyde: the activated enamine attacks the carbonyl carbon of the aldehyde and forms a β -hydroxy ester intermediate. (iv) Dehydration and cyclizations: the β -hydroxy-ester intermediate

undergoes dehydration, which creates a double bond between the α - and β -carbons, and finally, the dihydropyridine ring is generated through proton transfer and cyclization and generates the desired 1,4-DHP product.

Utilization of SSICG-12 for the Synthesis of 1,4-DHP-Based Drug Nemadipine B. In the category of drug molecules, 1,4-DHP-based drugs are especially important because of their structural similarities with NADH coenzymes, which play a key role in cellular energy production and are used to treat cardiovascular diseases.³⁴ Nemadipine B is a 1,4-DHPbased drug used to treat hypertension and angina by affecting the calcium flow in the blood and heart vessel cells.⁶² Here, the drug molecule nemadipine B was synthesized by using the most efficient catalyst, SSICG-12, under optimized Hantzsch conditions, where 2,3-dichlorobenzaldehyde was used as an aldehyde substrate (Figure 13). In the optimized condition, the reaction yielded a 96% isolated product, which was subsequently characterized by ¹H and ¹³C NMR (Figure S9j,k).

Catalytic Strecker Reaction. Motivated by the efficiency of the synthesized catalyst in the Hantzsch condensation reaction, we wanted to further explore the capacity of our catalyst in the Strecker reaction, which is a crucial reaction for synthesizing amino acids.³⁸ Herein, three components of the Strecker reaction have been studied by choosing benzaldehyde (1 mmol) as a model substrate, followed by a reaction with aniline





Figure 15. Optimization of the Strecker reaction by the catalyst SSICG-12, with respect to (a) time (kinetic study) and (b) amount of the catalyst (yields are calculated from ${}^{1}H$ NMR).



Figure 16. Synthesis of girgensohnine. Reaction conditions: 4-hydroxybenzaldehyde (1 mmol), piperidine (1 mmol), TMSCN (1.1 mmol), SSICG-12 (1 mol %). TON = 74; TOF = 74 h⁻¹.

(1 mmol) and trimethylsilyl cyanide (TMSCN) (1.1 mmol) at room temperature and solvent-free conditions (Figure 14); the progress of the reactions has been monitored by thin-layer chromatography. In room-temperature and solvent-free conditions, the efficiency of the precursor materials was initially examined, and a lower yield (<30%) was observed (Table S3 entries 1-4). In the same condition, the catalytic efficiency of SSICG-12 was tested, which gave a 100% NMR yield (97% isolated yield) in 1 h (Figure 15a) when 1 mol % of the catalyst was used (Table S3 entry 5) (Figure 15b) and analyzed by ¹H NMR spectra. In this optimized condition of the Strecker reaction, SSICG-11 and SSICG-13 give 93 and 67% NMR yields (90 and 66% isolated yields) (Table S3 entries 6–7) (Figure S10), respectively. It is worth mentioning that our synthesized adenine-based catalyst SSICG-12 shows better-to-comparable efficiency to some of the previously reported catalysts (Table **S4**).

Catalyst Recyclability and Substrate Scopes. The recyclability of SSICG-12 was tested up to the eighth cycle, and it maintained its efficiency and crystallinity, which was confirmed by ¹H NMR (Figure S11a) and PXRD (Figure S11b) analyses after each cycle. The ICP–MS experiment of the reaction mixture filtrate was performed for the leaching test, which showed a very negligible presence of cadmium (0.047 ppb), nullifying the indication of the catalyst leaching in the reaction medium. After the optimization of the model reaction, the efficiency of the catalyst (SSICG-12) was examined for a wide range of substituted aldehydes containing electrondonating ($-CH_3$ and $-OCH_3$) and -withdrawing groups (-Cl, -F, and -Br). It was observed that even though the yields are excellent in both cases, the substrates containing electron-withdrawing groups demonstrate higher yields in comparison to

electron-donating-group-containing substrates (Figure 12a-g). This phenomenon may be attributed to the electron density of the benzene ring being diminished by the presence of electronwithdrawing groups, thereby making the substrates more susceptible to nucleophilic attack by cyanide ions. Similar to the Hantzch condensation reaction, herein, bulky substrate 9anthracenecarboxaldehyde also does not show any considerable yield.

Mechanism. To better understand the relationship between the structure of our synthesized CPs and their efficiency, we have proposed a mechanism based on our results and reported literature (Figure S13). As the synthesized CPs lack significant porosity, the catalytic reaction primarily occurs on their surface.⁶¹ In the first step, the Lewis acidic site (activated metal center) of SSICG-12 interacts with the aldehyde and amine substrate and activates the substrates.^{32,53,63} Simultaneously, the Lewis basic sites (nitrogen sites of adenine) of the catalyst activate TMSCN by interacting with the Si of TMSCN.⁶⁴ In the second step, the activated benzaldehyde undergoes a nucleophilic addition with aniline, forming imine intermediates with the loss of a water molecule. In the next step, activated trimethyl cyanide reacts with the imine intermediate and forms α -aminonitrile with regeneration of the employed catalyst.

Utilization of SSICG-12 for the Synthesis of Piperidine-Based Natural Product Girgensohnine. Girgensohnine is a naturally occurring piperidine-based alkaloid.⁶⁵ This natural product is generally extracted from the *Girgensohnia oppositiflora* shrub, which provides a very low yield (less than 0.05%).⁴³ After establishing the catalytic efficiency of SSICG-12 in a wide range of substrates, it was utilized to synthesize the alkaloid girgensohnine under optimized condition conditions where 4-



Figure 17. Catalytic efficiency of synthesized CPs in the (a) Hantzsch condensation reaction and (b) Strecker reaction (yields are calculated from 1 H NMR); (c–e) metal coordination center of SSICG-11–13.

hydroxybenzaldehyde was used as the aldehyde substrate, and piperidine was used as an amine substrate (Figure 16), resulting in a 74% isolated yield (Figure S14).

Critical Analysis of Catalytic Efficiency. As discussed earlier, the synthesized CPs SSICG-11-13 show different efficiencies in both the Hantzsch and Strecker reactions (Figure 17a,b). However, the trend of their efficiency is similar in both cases (efficiency SSICG-12 > SSICG-11 > SSICG-13). The dissimilar efficiency of the CPs has been analyzed by correlating our experimental results (Table S5) with the previous reports and can be explained by the following two major points: (i) the presence of coordinated water: SSICG-11 and 12 both have coordinated water molecules, which can reversibly be removed by the activation process to create an unsaturated, efficient Lewis acidic metal center [open metal sites (OMS)]. These OMSs are a major contributor to their superior catalytic efficiencies as they enhance reactivity by metal unsaturation, which provides higher exposed active sites, stronger binding ability with the substrate, and coordination flexibility (Figure 17c,d).^{43,47,66-68} On the other hand, there are no coordinated water or labile solvent molecules in the structure of SSICG-13. As a result, it shows significantly lower efficiency in both catalytic reactions (Figure 17e) because metal unsaturation (OMS) cannot be created through a simple activation procedure. (ii) The presence of higher Lewis basic sites: among SSICG-11 and 12, SSICG-12 contains a higher amount of Lewis basic sites (adenine moiety), which facilitates the higher efficiency of SSICG-12 (Figure 17c,d).^{54,69,70}

CONCLUSIONS

In conclusion, this work demonstrates the successful synthesis of three distinct adenine-based CPs (SSICG-11-13) through controlled variation of metal ion, acid ligand (H₂NIPA), and adenine (Ad) concentrations. These three synthesized CPs exhibit unique structural features with distinctly different unit cells. The materials are readily synthesizable on a bulk scale, which was confirmed by PXRD. The unique structural features of these three CPs lead to dissimilar properties, such as surface area and CO₂ adsorption capacities. The synthesized CPs, SSICG-11-13, contain both Lewis acidic and basic centers, and for that, it was utilized as a heterogeneous catalyst in Hantzsch and Strecker reactions. Interestingly, each of the three catalysts shows different catalytic activity (SSICG-12 > SSICG-11 ≫ SSICG-13). This different catalytic activity of the three adeninebased CPs is thoroughly analyzed in this study by correlating the synergistic amalgamation of coordinative unsaturation and Lewis basic sites in their structures, which will pave the way for further exploration of stoichiometric tuning to optimize the structure and catalytic efficiency of CPs. The CP-catalyzed synthesis of drug molecules and natural products is a rapidly evolving area of research with significant potential. In our study, the most efficient catalyst, SSICG-12, was utilized to synthesize a calcium blocker, nemadipine B, by the Hantzsch reaction and a natural product, girgensohnine, by the Strecker reaction with good yields.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c04161.

Detailed synthetic and catalytic procedures; crystal information table; structural analysis; and PXRD, FE-SEM, and NMR spectra of the catalytic reactions (PDF)

Accession Codes

Deposition numbers 2360322–2360324 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

The authors declare no competing financial interest.

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