ABSTRACT: Covalent organic frameworks (COFs) are an emerging class of crystalline porous polymers with tailor-made structures and functionalities. To facilitate their utilization for advanced applications, it is crucial to develop a systematic approach to control the properties of COFs, including the crystallinity, stability, and functionalities. However, such an integrated design is challenging to achieve. Herein, we report supramolecular strategy-based linkage engineering to fabricate a versatile 2D hydrazone-linked COF platform for the coordination of different transition metal ions. Intra- and intermolecular hydrogen bonding as well as electrostatic interactions in the antiparallel stacking mode were first utilized to obtain two isoreticular COFs, namely COF−DB and COF−DT. On account of suitable nitrogen sites in COF−DB, the further metalation of COF−DB was accomplished upon the complexation with seven divalent transition metal ions M(II) (M = Mn, Co, Ni, Cu, Zn, Pd, and Cd) under mild conditions. The resultant M/COF−DB exhibited extended π-conjugation, improved crystallinity, enhanced stability, and additional functionalities as compared to the parent COF−DB. Furthermore, the dynamic nature of the coordination bonding in M/COF−DB allows for the easy replacement of metal ions through a postsynthetic exchange. In particular, the coordination mode in Pd/COF−DB endows it with excellent catalytic activity and cyclic stability as a heterogeneous catalyst for the Suzuki−Miyaura cross-coupling reaction, outperforming its amorphous counterparts and Pd/COF−DT. This strategy provides an opportunity for the construction of 2D COFs with designable functions and opens an avenue to create COFs as multifunctional systems.

INTRODUCTION

Covalent organic frameworks (COFs) are a class of crystalline porous polymers constructed by reticulating organic subunits into extended one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) structures via covalent bonds.1−4 Benefiting from the seminal work of Yaghi et al. in 2005,5 numerous COFs have been developed and have shown great potential in a wide variety of fields, including gas capture and separation,6−9 energy storage,10−12 optoelectronics,13−16 sensing,17−19 catalysis,20−23 environmental remediation,24−27 and biomedicine.28−30 Among all COFs, the synthesis of 2D COFs is governed by both the lateral extension of the organic monolayer via a covalent bond and the vertical stacking of conjugated multilayers through noncovalent forces, endowing them with periodic columnar π-arrays and open 1D channels.31−33 The selection of appropriate linkers and linkages and their stacking modes provides efficient ways to tailor the structures and functionalities of 2D COFs at the atomic scale. In particular, the linkage chemistry is crucial for the design of 2D COFs because highly ordered structures often rely on the formation of reversible linkages to connect organic linkers through thermodynamic equilibria.34−36 Such a feature allows for the formation of crystalline COFs through dynamic error correction. However, the same feature also impairs the stability of COFs toward solvents and chemicals. For example, imine-linked COFs have both good reversibility and functional compatibility under solvothermal conditions but are susceptible to decomposition or exfoliation under acidic or alkaline aqueous conditions.37,38 Beyond the role of bridging the
linkers, the types and conformation of linkages also have a pronounced influence on the properties of COFs, such as their magnetic, electronic, and optical properties. Significant efforts have been devoted to strengthening the stability of the frameworks through the covalent modification of the linkages. Some 2D COFs with linkages such as amide, thiazole, oxazole, amine, cyclic carbamate and thiocarbamate, thieno[3,2-c]pyridine, quinoline, tetrahydroquinoline, and α-aminonitrile have been obtained with enhanced chemical stability and improved π-electron conjugation. However, the resultant COFs often suffer from decreased porosity, an irreversible transformation, and limited functionalities. These unsatisfactory aspects suggest that the covalent modification of linkages is not an optimal strategy for improving the crystallinity, stability, and functionality of 2D COFs.

The utilization of noncovalent or supramolecular interactions for the linkage engineering provides an alternative general approach for the synthetic control of 2D COFs. Different from covalent bonding, supramolecular interactions feature reversible bonding behavior upon external stimuli. Recent explorations have revealed that the introduction of appropriate noncovalent interactions, such as intra- or intermolecular hydrogen bonding, molecular dipole moments, hydrophobic interactions, and donor–acceptor (D–A) interactions, are capable of tuning the porosity, stability and stacking behavior of 2D COFs. To the best of our knowledge, however, one of the most widely known supramolecular interactions, i.e., metal coordination, was barely utilized to improve the porosity and stability of 2D COFs. Although numerous examples have demonstrated that 2D COFs can serve as host materials to chelate metallic guests, very little attention has been paid to how different coordination modes of the metal-binding units (such as the nitrogen atom) in 2D COFs could affect the properties of the resulting materials. Three coordination modes between the metal-binding units and the metal species have been well established using 2D COFs as scaffolds thus far (Scheme 1a–c). However, these coordination modes often introduce catalytically active sites into COFs at the expense of decreased crystallinity and porosity. This dilemma can be circumvented by introducing the fourth coordination mode where metal species are coordinated with metal-binding units distributed at the linker and linkage to form a five-membered ring conjugation within the linkages (Schemes 1d and 2). Such a distinct coordination mode restricts the bond rotation of the linkage to allow for extended π-electron conjugation in 2D COFs. This arrangement would also enhance the interlayer interactions and introduce additional functionalities to the resultant frameworks.

Herein, we developed a linkage engineering strategy based on the supramolecular principle to fabricate a versatile 2D hydrazone-linked COF platform for the coordination of seven transition metal ions. The resultant materials feature a combination of extended π-conjugation, improved crystallinity, enhanced stability, and additional functionalities. This outcome was realized by restricting the bond rotation of linkages in a stepwise fashion by taking advantage of multiple supramolecular interactions. We first fabricated two 2D hydrazone-linked COFs (i.e., COF–DB and COF–DT) with antiparallel stacking in which the linkages were partially restricted by intramolecular and intermolecular hydrogen bonding as well as electrostatic interactions. Benefiting from its unique coordination mode, the porosity and stability of COF–DB were further improved through metal coordination, which simultaneously endowed the ensuing metalated COF–DB (denoted as M/COF–DB) with additional functionalities. In addition, metal ions confined within the open channels of

Scheme 1. Different Coordination Modes between Metal-Binding Units and Metal Species in 2D COFs

“Transition metals are coordinated with metal-binding units (such as nitrogen atoms) distributed at (a) linkages (ref 20), (b) linkers or linkages (ref 58), (c) linkers (ref 59), and (d) linkers and linkages (this work). Noncovalent interactions are presented in the local region of the frameworks for better visibility.
M/COF−DB can be readily replaced via a postsynthetic metal exchange. In particular, Pd/COF−DB showed enhanced activity and recycling stability for the Suzuki−Miyaura cross-coupling reaction in comparison with its amorphous counterparts and Pd/COF−DT. This approach not only lays a solid foundation for the development of 2D COFs toward advanced applications but also provides an inspiration for the design of functionalized COFs through supramolecular interactions.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization.** As shown in Scheme 2, two types of hydrazides with and without methoxy groups, i.e., 2,5-dimethoxyterephthalohydrazide (DMTHA) and terephthalohydrazide (THA), were selected as linear ditopic linkers. Two kinds of aldehydes sharing identical chemical compositions but different positions of the nitrogen atoms, i.e., 5,5′,5″-(benzene-1,3,5-triyl)tripicolinaldehyde (BTTPA) and 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)tribenzaldehyde (TATTA), were used as triangular tritopic linkers. Theoretically, we would be able to prepare four kinds of 2D hydrazone-linked COFs through the permutation of these linkers. To our delight, we successfully synthesized two isoreticular COFs, namely COF−DB and COF−DT, via an acid-catalyzed solvothermal polycondensation reaction of DMTHA with BTTPA and TATTA, respectively (see the Supporting Information for synthetic details). Attempts to yield the other two COFs only resulted in the formation of amorphous polymers, suggesting the important role of intramolecular hydrogen bonding in facilitating the crystallization of COFs. Various synthetic conditions were extensively screened to optimize the
The as-prepared COFs were first assessed by Fourier-transform infrared (FT-IR) spectroscopy. In the FT-IR spectra, the stretching vibration bands at 1655 and 1658 cm\(^{-1}\) assigned to the newly formed C=N bonds were clearly observed for COF−DB and COF−DT, respectively. They were identical to their respective model compounds, suggesting the successful formation of hydrazone moieties from the polycondensation of the amino groups of DMTHA with the aldehyde groups of BTTPA or TATTA. The FT-IR spectra also showed that the stretching vibration bands of the amino groups from DMTHA (\(\nu_{as-NH_2}, 3298 \text{ cm}^{-1}\); \(\nu_{s-NH_2}, 3204 \text{ cm}^{-1}\)) and the aldehyde groups from BTTPA (HC = O, 1706 cm\(^{-1}\)) or TATTA (HC = O, 1704 cm\(^{-1}\)) were dramatically attenuated after polycondensation, indicating a considerably high degree of polymerization (Figure 1a and b). The compositions of COF−DB and COF−DT were then investigated by X-ray photoelectron spectroscopy (XPS). Three intense peaks corresponding to C 1s, O 1s, and N 1s signals were observed in the XPS patterns of the two COFs, and their high resolution XPS spectra firmly supported the formation of hydrazone bonds (Figures S1 and S2).

The atomic scale construction of the two COFs was further confirmed by solid-state cross-polarization with magic angle spinning (CP/MAS) \(^{13}\text{C}\) NMR spectroscopy. The characteristic resonance signals attributed to the chemical shift of the C=N bonds were observed at 146 and 150 ppm for COF−DB and COF−DT respectively, which provided overwhelming evidence for the formation of hydrazone linkages. The resonance signals of other carbon atoms, including the methyl and phenyl groups, were in accordance with their chemical structures (Figure 1c and d).

Thermogravimetric analysis (TGA) revealed that the low-temperature onsets for the first derivatives of the traces were at 305 and 351 °C for COF−DB and COF−DT, respectively (Figure S3), indicating they both had a high thermal stability. Field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) verified the phase purity of COF−DB and COF−DT, which revealed highly uniform coral-like and fiber-like morphologies, respectively (Figures S4 and S5).

Crystalline structures of the two COFs were also elucidated by powder X-ray diffraction (PXRD) analysis with Cu Kα radiation. As shown in Figure 2, a strong diffraction peak corresponding to the (100) facet was observed at 2.33° in the experimental PXRD profile of COF−DB, which indicated that it possessed a long-range ordered structure. In addition to the (100) facet, diffraction peaks at 4.09, 4.78, 6.34, 8.12, 14.13, 16.38, and 25.80° were attributed to the (110), (200), (210), (220), (600), (411), and (001) facets, respectively. The
successful synthesis of COF−DB was also corroborated by small and wide-angle X-ray scattering (SAXS/WAXS) experiments (Figures 1e and S6), suggesting the highly crystalline nature of the structure. The high-resolution TEM image revealed that COF−DB had a 2D layered structure with an interlayer distance of approximately 3.3 Å (Figure 1f), which was consistent with the π−π stacking distance obtained from the PXRD data. For COF−DT, the most intense diffraction peak assigned to the (100) facet appeared at 2.29°, while other diffraction peaks at 4.03, 4.70, 6.20, 8.19, 10.31, and 26.42° were assigned to the (110), (200), (210), (310), (410), and (001) facets, respectively.

To determine the exact structures of the two COFs, three proposed structures based on antiparallel, eclipsed, and staggered stacking were simulated by density functional theory (DFT) and universal force field calculations. The staggered structures could be ruled out by comparing the experimental and simulated PXRD patterns from 10 to 15°, whereas the
simulated PXRD patterns of the antiparallel and eclipsed structures were in line with the experimental ones. Recent studies have suggested that intramolecular and intermolecular hydrogen bonding could promote the crystallization of hydrazone-linked COFs, and the dipole moments of C-$(\delta^-)$=O$(\delta^-)$ and O$(\delta^-)$=R$(\delta^-)$ could induce adjacent layers to preferably adopt antiparallel stacking.\textsuperscript{56,60} Thus, we then compared DFT-optimized COF–DB and COF–DT structures in both antiparallel and eclipsed stacking. The total energy of the antiparallel-stacked structures was 3.62 and 3.06 eV per unit cell (containing two layers) more stable than that of eclipsed stacked ones for COF–DB and COF–DT, respectively. The $\pi$-$\pi$ interlayer distances simulated by DFT and universal force field calculations for the antiparallel-stacked structures were 3.5–3.6 Å, whereas those for the eclipsed-stacked structures were $\sim$3.8 Å, also indicating that the antiparallel-stacked structures agreed better with the experimental PXRD results (Table S1). Besides reducing the electrostatic repulsion between atomic species with similar partial charges, the antiparallel stacking also favors the formation of interlayer hydrogen bonding. Specifically, Figures S7 and S8 show antiparallel stacking results in a redistribution of the charge with the O atom in the C=O group gaining more electrons, thus strengthening the interlayer hydrogen bonding marked by “b” and “c” in Figure 2e. The existence of intralayer N-H···O (2.070/2.063 Å) and interlayer N-H···O (2.343/2.429 Å) as well as C-H···O (2.920/3.040 Å) hydrogen bonding in the antiparallel-stacked structures for COF–DB/COF–DT restricts the molecular bond rotation, thus facilitating the crystallinity of these COFs. These results strongly suggest that both COF–DB and COF–DT adopt antiparallel stacking facilitated by intralayer and interlayer hydrogen bonding as well as electrostatic interactions. The experimental PXRD patterns for COF–DB and COF–DT agree well with the predicted ones generated from the antiparallel stacking model belonging to the P6$_3$22 space group. The unit cell parameters of two COFs were optimized by Pawley refinement to give good results as follows: a = b = 41.95 Å, c = 7.23 Å, $\alpha = \beta = 90.00^\circ$ and $\gamma = 120^\circ$, with R$_{wp}$ = 2.99% and R$_p$ = 2.33% for COF–DB; a = b = 43.12 Å, c = 7.28 Å, $\alpha = \beta = 90.00^\circ$ and $\gamma = 120^\circ$, with R$_{wp}$ = 2.96% and R$_p$ = 2.48% for COF–DT. As revealed by the difference plots (Figure 2, gray curves), the refined results are consistent with the predicted unit cell parameters.

The permanent porosity of COF–DB and COF–DT was assessed by N$_2$ adsorption–desorption experiments at 77 K. COF–DB showed sharp uptake below $P/P_0 = 0.01$ with a step between $P/P_0 = 0.01–0.35$, which was in good agreement with the type IV sorption model for mesoporous materials.\textsuperscript{61} COF–DT exhibited a similar nitrogen adsorption isotherm as well (Figure S9). The Brunauer–Emmett–Teller (BET) specific surface areas were calculated using the adsorption data within the 0.15 $< P/P_0 < 0.30$ range to give 632 and 747 m$^2$ g$^{-1}$ for COF–DB and COF–DT, respectively (Figures S10 and S11). A nonlocal density functional theory (NLDFT) model was applied to the isotherms of COF–DB and COF–DT to estimate their pore size distributions and total pore volumes. A narrow pore size distribution with an average pore width of 31 Å was observed for both COFs (Figure S9), which was in good agreement with the theoretical pore sizes of the hexagonal
pores (ca. 35 Å). The total pore volumes of COF–DB and COF–DT were estimated to be 0.49 and 0.20 cm³ g⁻¹, respectively, at P/P₀ = 0.99.

Stability of COF–DB upon Exposure to Various Solvents. To assess the chemical stability of COF–DB, the as-prepared COF–DB sample was soaked in various solvents under ambient conditions for 48 h, including tetrahydrofuran (THF), CHCl₃, toluene, CH₃OH, 1,4-dioxane, dimethylformamide (DMF), and H₂O. As indicated in the PXRD profiles, the samples dispersed in THF, CHCl₃, toluene, CH₃OH, and 1,4-dioxane could preserve the crystalline structures, while those exposed to DMF and H₂O showed a loss of the bulk crystallinity (Figure S12). The FT-IR spectra of samples immersed in various solvents exhibited characteristic peaks corresponding to the hydrazone moieties, which were almost identical to those of the parent COF–DB (Figure S13). These experimental results demonstrated that hydrazone-linked COF–DB was chemically stable in most solvents, and the apparent loss of crystallinity should be attributed to the exfoliation of multilayers rather than the hydrolysis of covalent hydrazone linkages in COF–DB. A similar phenomenon was also demonstrated by Dichtel et al.⁶² The easy exfoliation of hydrazone-linked COF–DB in H₂O or DMF should be ascribed to the partial bond rotation of linkages in the 2D extended network, leading to relatively weak interlayer interactions. We envisioned that introducing the coordination interactions with metal ions could further restrict the bond rotation of linkages and lock the 2D sheets in a more planar conformation. This arrangement would not only increase the degree of π-conjugation in the 2D networks but also enhance the stacking interactions over the 2D sheets.

Improved Porosity and Stability Promoted by Metal Coordination. The structural design of COF–DB allows it to act as a versatile platform for the chelation of a metallic species. Toward this goal, we carried out the metalation of COF–DB with different metal ions, which could be easily realized by immersing COF–DB in saturated solutions containing M²⁺ salts (M = Mn, Co, Ni, Cu, Zn, Pd, and Cd). A distinct color change was observed for the resultant M/COF–DB samples. The unchanged PXRD patterns of M/COF–DB proved that the ordered structure of COF–DB was well preserved after the metalation (Figure 3a). The interactions between COF–DB and various metal ions were further investigated by FT-IR spectroscopy. In comparison with the FT-IR spectrum of parent COF–DB for the C=N stretching vibration (1655 cm⁻¹), an obvious blue shift was observed in the spectra of M/COF–DB, ranging from 1657 to 1663 cm⁻¹, suggesting the coordination of the metal species at the chelation site (Figure S14). The SEM images showed that M/COF–DB possessed similar morphologies to the parent COF–DB (Figure S15). Notably, the even distribution of metal ions in the samples was confirmed by the scanning electron microscope energy-dispersive X-ray spectra (SEM-EDS, Figure S16). The well-dispersed metal species (black dots) could be clearly observed in the TEM images as well (Figure S17). The metal contents of the M/COF–DB samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (Table S2). These data provided compelling evidence for the strong coordination of metal ions with the metal-binding units in COF–DB.

The porosity of M/COF–DB was assessed by nitrogen adsorption–desorption experiments. As shown in Figure 3c, the adsorption isotherms of M/COF–DB were almost identical to those of the parent COF–DB, with a type IV sorption profile. The pore sizes of M/COF–DB were approximately 31 Å as well (Figure S18). Notably, the BET surface areas of M/COF–DB were higher than that of the parent COF–DB (632 m² g⁻¹), ranging from 728 to 1047 m² g⁻¹ (Figures S19–S25). The significant improvement in the specific surface area and negligible change in the pore size distribution for M/COF–DB suggested that the introduction of the metal species did not block the mesoporous channels, while improving the regularity of the resultant frameworks.

The influence of metal coordination on the stability of the frameworks was also investigated. The M/COF–DB samples were examined by PXRD again after incubating in H₂O or DMF under ambient conditions for 48 h. The PXRD patterns of six M/COF–DB samples except Cd/COF–DB were well preserved, suggesting that the layered stacking structures of the M/COF–DB were well retained without the exfoliation upon exposure to H₂O and DMF (Figures S26 and S27). TGA curves also revealed that these M/COF–DB samples had a better thermostability than the parent COF–DB (Figure S28).

To highlight the unique advantages of metal coordination in M/COF–DB, Pd/COF–DT and amorphous Pd/COF–DB were selected and synthesized as representative models for comparison (Figure S29). The SEM and TEM images revealed that, after the coordination with Pd(OAc)₂, the morphologies became more aggregated for both samples (Figures S4 and S5). Amorphous Pd/COF–DB showed an increased BET surface area (192 m² g⁻¹) and optimized pore size distribution as compared with amorphous COF–DB (48 m² g⁻¹), whereas the BET surface area of Pd/COF–DT (342 m² g⁻¹) was found to be lower than that of COF–DT (747 m² g⁻¹) with the preservation of the pore size distribution (Figures S30–S34). The thermal stability of Pd/COF–DT showed a negligible change after the metalation of COF–DT (Figure S35). The above results suggested that different coordination modes did exert significant an influence on the porosity and stability of the resultant frameworks.

Influence on the Properties of Different 2D COFs Exerted by Metal Coordination. To get deeper insight into the improved porosity and stability promoted by the metal coordination, two model compounds, DB and DT (see the Supporting Information for their chemical structures and synthetic details), were first synthesized to investigate their different coordination modes in Pd(II)/DB and Pd(II)/DT. ¹H NMR spectroscopy was carried out in DMSO-d₆. Upon the addition of Pd(OAc)₂, a new set of resonance peaks was clearly observed besides free DB, suggesting the occurrence of strong interactions between DB and Pd(II) in forming a Pd(II)/DB complex. In contrast, the addition of Pd(II) into a solution of DT produced a negligible change in the chemical shift, implying that the interactions between DT and Pd(II) were very weak (Figures S36 and S37). To obtain more information on the structural change caused by the metal coordination, the photophysical properties of DB and DT before and after coordinating with Pd(OAc)₂ were also recorded by UV/vis spectroscopy. Both DB and DT exhibited three absorption bands at 309, 320, and 348 nm, suggesting that DB and DT possessed a similar degree of π-electron delocalization before the coordination with the metal species. Upon adding Pd(OAc)₂ to the solutions containing the two model compounds separately, no noticeable shift was observed in the UV/vis spectrum of Pd(II)/DT as compared to that of free DT, whereas the maximum absorption band of Pd(II)/DB
exhibited a large red shift to 500 nm from 348 nm in free DB. The magnitude of the bathochromic shift is approximately 150 nm, which could be ascribed to the formation of a greater degree of π-conjugation via the coordination with Pd(OAc)₂. A remarkable visible color change from colorless to yellow was also observed (Figure S38). Such a phenomenon could be attributed to different coordination modes between the organic ligands and metal ions. The main feature of DB lies in its distinct coordination mode through the pyridine and hydrazone nitrogen atoms to serve as a bidentate ligand to form a five-membered ring conformation upon complexation with a metal species. This complexation mode can effectively increase the degree of π-conjugation of the system. Compound DT, on the other hand, only depends on the nitrogen atoms of the hydrazone linkages to form a sandwich-like structure with metal ions, which had hardly any influence on the degree of π-electron delocalization.

A similar phenomenon was also observed for π-conjugated COFs, and these interactions between metal-binding units and metal ions were further amplified to exert an important influence on the properties of the resulting materials. The lowest-energy absorption band of Pd/COF–DB red-shifted to a larger extent as compared to that of Pd/COF–DT, resulting in a distinct color change from yellow to red (Figures 3a and S39). The difference could be ascribed to the different coordination modes between Pd/COF–DB and Pd/COF–DT. For M/COF–DB, such as Pd/COF–DB, the metal species coordinated with the metal-binding units (nitrogen atoms) distributed at linkers and linkages could suppress the bond rotation of the linkages and lock the hexagonal 2D sheets in a more planar conformation. This arrangement could be verified by comparing the PXRD patterns of COF–DB and M/COF–DB. The presence of the diffraction peak assigned to the (001) facet revealed that the M/COF–DB samples had an ordered arrangement of multilayers, which corresponded to the π–π stacking distance between adjacent layers. The π–π stacking distance in all M/COF–DBs, ranging from 3.43 to 3.35 Å, was smaller than that of the parent COF–DB (3.45 Å) (Figure 3b). Therefore, M/COF–DBs should have more compact structures as a result of the synergistic supramolecular interactions that increased the stacking interactions between adjacent 2D layers in M/COF–DB, leading to extended π-conjugation, improved crystallinity, and enhanced stability. By contrast, the π–π stacking distance of M/COF–DTs, ranging from 3.37 to 3.38 Å, was slightly larger than that of the parent COF–DT (3.37 Å) (Figure S39). This result suggests that the introduction of the routine coordination mode, where metal species coordinate with metal-binding units (nitrogen atoms) distributed at the linkages, could only weaken the interlayer interactions to some extent. The loosely stacked layers may account for the obvious decrease of the crystallinity and stability of Pd/COF–DT.

**Postsynthetic Metal Exchange.** The dynamic nature of coordination bonding inspired us to explore the possibility of metal exchange in M/COF–DB. M/COF–DB (M = Mn and Co) samples were selected and immersed in saturated solutions containing Pd(II) at ambient conditions for 12 h. The successful transformation of M/COF–DB (M = Mn and Co) into M′/COF–DB (M′ = Pd) was demonstrated by the dramatic change in the color of the samples and a negligible difference in the PXRD patterns (Figure S40). SEM-EDS analysis also revealed the homogeneous distribution of Pd(II) ions in the exchanged Pd/COF–DB sample, indicating that most of the Mn(II) or Co(II) was readily replaced by Pd(II) ions under mild conditions (Figures S41 and S42). Thus, these results suggested that COF–DB might serve as a promising and versatile platform to obtain different metalated COFs through a postsynthetic metal exchange.

**Heterogeneous Catalysis for the Suzuki–Miyaura Cross-Coupling Reaction.** The development of recyclable heterogeneous catalytic systems is the impetus for many industrial applications. In terms of their practical use, heterogeneous catalysts outperform their homogeneous counterparts due to their easy separation from reaction mixtures and efficient performance in continuous flow processes. The metalated COFs may serve as promising systems for heterogeneous catalytic reactions. Given its good crystallinity, stability, and functionality, Pd/COF–DB was selected as a heterogeneous catalyst to investigate the Suzuki–Miyaura cross-coupling reaction, which was well-known as a useful method to form C–C bonds. As presented in Table 1, all electron-donating (entry 3) and electron-withdrawing (entry 4) aryl iodide substrates gave rise to the expected biaryl products in excellent yields (95–99%) within 30 min (entries 1–4). Similarly, high yields (95–99%) could also be obtained for the less active aryl bromides (entries 5–9), suggesting the superb efficiency of Pd/COF–DB for the Suzuki–Miyaura reaction.

The recyclability and durability of Pd/COF–DB was further assessed by subjecting it to four consecutive catalytic cycles using bromobenzene and phenylboronic acid as reactants. It was found that the catalytic activity of Pd/COF–DB could be well maintained at a high level. However, Pd/COF–DT and amorphous Pd/COF–DB showed a significant loss of catalytic activity after four cycles of testing, although their fresh catalysts exhibited good catalytic activities (Figure S43). The well-preserved ordered structure of the recycled Pd/COF–DB was also verified by PXRD and SEM analysis, showing an insignificant decrease in the diffraction intensity and an almost unchanged morphology. In contrast, a significant decrease in the intensity of the PXRD pattern was observed for both Pd/COF–DT and amorphous Pd/COF–DB, suggesting their lower stability compared to Pd/COF–DB (Figure S44).
low stability of Pd/COF–DT and amorphous Pd/COF–DB was further supported by the aggregated morphologies from SEM images (Figure S45). We then conducted a leaching experiment to demonstrate that the reaction was indeed catalyzed under heterogeneous conditions. Pd/COF–DB was refluxed under the same reaction conditions in the absence of reactants. ICP-AES analysis of the filtrate showed that less than 1.0 ppm of Pd content was detected, indicating that the coordination of Pd(OAc)₂ with COF–DB is strong enough and the catalytic reaction proceeds through a heterogeneous process. Based on the experimental results and previous reports,⁶³,⁶⁴ a plausible reaction mechanism for the formation of biaryls catalyzed by Pd/COF–DB is outlined in Figure S46.

The superior catalytic activity and stability of Pd/COF–DB could be attributed to the unique coordination mode after the introduction of the metal species. Pd/COF–DB preserves its periodic columnar arrays and 1D open mesopore channel well, providing easy access to the active sites as well as the fast diffusion of the reactants and products. In addition, the ICP-AES analysis showed that the Pd content in Pd/COF–DB was 3.1× higher than that of Pd/COF–DT (Table S3), indicating higher Pd loading for the former. Therefore, the coordination mode in Pd/COF–DB not only serves as a noncovalent force to stabilize the ordered structure but also facilitates the binding of more metal ions on the COF scaffold for better catalytic efficiency. The crystallinity, stability, and functionality can be simultaneously integrated into Pd/COF–DB through the combination of synergistic supramolecular interactions.

**CONCLUSION**

We have successfully developed a supramolecular strategy to conduct linkage engineering to fabricate a versatile 2D hydrazone-linked COF platform, demonstrating that different coordination modes have a significant influence on the properties of the resultant frameworks. Experimental and computational studies reveal that inter- and intramolecular hydrogen bonding as well as electrostatic interactions in dipole-induced antiparallel stacking work together to partially restrict the bond rotation of linkages within 2D COFs, laying the foundation for the successful synthesis of COF–DB and COF–DT. The bond rotation of the linkages in COF–DB can be further restricted through the metal coordination, leading to a more rigid and stable linkage conformation. This conformation greatly improves the planarity of the 2D sheets and strengthens the interlayer interactions. Furthermore, COF–DB can serve as a versatile platform to chelate seven different divalent transition metal ions under mild conditions. The resultant M/COF–DB samples exhibit extended π-conjugation, improved crystallinity, enhanced stability, and additional functionalities relative to the parent COF–DB. In addition, metal ions anchored on the ordered channel walls of M/COF–DB can be readily replaced via a postsynthetic metal exchange. On account of the synergistic supramolecular interactions, Pd/COF–DB shows excellent catalytic activity and stability for the Suzuki–Miyaura cross-coupling reaction as compared to its amorphous counterparts and Pd/COF–DT. This work provides inspirations to design 2D COF-based platforms for diverse applications. We believe that the supramolecular design strategy described herein would complement the existing covalent modification approach and promote the further development of 2D COFs for more advanced applications.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c08436.

Experimental procedures, characterization data, supplemental figures, and computational details (PDF)

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