Metal–Organic Frameworks Hot Paper

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Chiral Frustrated Lewis Pair@Metal-Organic Framework as a New Platform for Heterogeneous Asymmetric Hydrogenation

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Abstract: Asymmetric hydrogenation, a seminal strategy for the synthesis of chiral molecules, remains largely unmet in terms of activation by non-metal sites of heterogeneous catalysts. Herein, as demonstrated by combined computational and experimental studies, we present a general strategy for integrating rationally designed molecular chiral frustrated Lewis pair (CFLP) with porous metal–organic framework (MOF) to construct the catalyst CFLP@MOF that can efficiently promote the asymmetric hydrogenation in a heterogeneous manner, which for the first time extends the concept of chiral frustrated Lewis pair from homogeneous system to heterogeneous catalysis. Significantly, the developed CFLP@MOF, inherits the merits of both homogeneous and heterogeneous catalysts, with high activity/enantio-selectivity and excellent recyclability/regenerability. Our work not only advances CFLP@MOF as a new platform for heterogeneous asymmetric hydrogenation, but also opens a new avenue for the design and preparation of advanced catalysts for asymmetric catalysis.

Introduction

Asymmetric catalysis has been extensively exploited to synthesize chiral molecules, which are valuable in medicine, agriculture, and daily necessities.[1] One of the well-known reactions, asymmetric H_2 hydrogenation, has already been industrialized because of its significance and convenience.[2] So far, various strategies have been conceived to prepare catalysts for both homogeneous and heterogeneous asymmetric hydrogenation. In particular, molecular chiral catalysts with metal/non-metal active sites are known to be highly active,[3] but they have some issues with catalyst-product separation and catalyst reuse. As for heterogeneous catalysts, they are recyclable and beneficial in achieving good selectivity;[4] however, currently all developed strategies require the employment of noble metal/transition metal as active sites along with the synthesis of complicated chiral ligand, especially for catalysts derived from porous chiral supports. To reduce the cost as well as to ensure recyclability, an operationally-simple strategy to prepare porous support with non-metal active sites (Figure 1) is highly desired; which, however, has not been achieved. This gap could be bridged by combining the frontier of chemistry with advanced materials.

The concept of "Frustrated Lewis Pair" (FLP) was conceived in 2006 to describe the frustration (steric hindrance) between a Lewis acid and a Lewis base that could promote H_2 activation under mild conditions.[5] The classic FLP catalysts are typically based on main-group elements, with bulky B compounds acting as the Lewis acids and bulky N/P compounds acting as the Lewis bases, and have attracted great attention because such a non-metal strategy can realize H_2 activation that noble metal and transition metal catalysts previously achieved.[3a–c] Subsequently, substantial FLPs for the activation of small molecules such as olefins, alkynes, and CO_2 have been developed with significant progresses made in recent years.[6] Some examples have been illustrated to verify the feasibility of using molecular chiral FLPs (CFLPs) for homogeneous asymmetric hydrogenation.[3d–g] To date, three strategies for

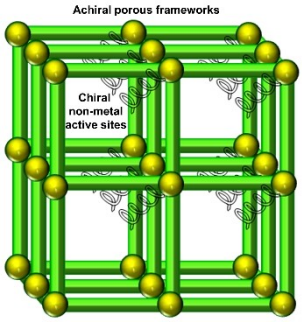

Figure 1. An illustration of recyclable catalysts for asymmetric hydrogenation derived from achiral porous frameworks and chiral non-metal active sites.

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the construction of molecular CFLPs catalysts have been proposed: (i) intramolecular CFLPs, which usually are tedious to design and synthesize;[7] (ii) sterically demanding chiral Lewis acid paired with sterically demanding achiral Lewis base, which has been investigated mostly;[8] (iii) sterically demanding achiral Lewis acid coupled with sterically demanding chiral Lewis base, which has been rarely developed.[9] Moreover, the bifunctional Lewis acid/Lewis base, which may be helpful for post-modification has not been developed in CFLPs. Furthermore, the recyclability and catalyst-product separation issues for CFLPs catalysts have yet to be tackled.

To obtain a recyclable FLP catalyst, methods including post-modification and in situ generation of achiral molecular FLPs on/in various supports have been gradually established.[10] The porous crystalline frameworks with large surface areas, uniform pores, and high stability, can stand out from various supports investigated thus far.[11] In this context, MOFs, which consist of metal nodes coordinated to organic ligands to form three-dimensional (3D) framework structures featuring tunability in design and function, are particularly appealing.[12] Indeed, we recently demonstrated the successful incorporation of FLPs into MOFs; and the MOF not only can stabilize FLPs with improved catalysis performances, but also render FLPs with interesting size/stereo/chemo selectivities which were not observed in the homogeneous systems.[13] Based on these successes, we aim to expand FLP@MOF for heterogeneous asymmetric catalysis, which has not been achieved for porous support-based FLP catalysts.[14]

Instead of employing chiral MOFs[4b–g] which have been extensively developed for asymmetric catalysis, our approach lies in the incorporation of CFLPs into achiral MOFs, which not only can avoid the tedious synthesis of chiral ligands to construct chiral MOFs but also can allow facile control of the catalysis performance of resultant CFLPs@MOFs by changing the type and amount of CFLPs. In this work, we focus on incorporating various types of CFLPs into MOF for asymmetric hydrogenation and demonstrate how the computational studies on the rationally designed CFLPs can guide the construction of CFLP@MOF system with optimal catalysis performance.

Results and Discussion

It's been documented that open metal sites can render MOFs with excellent performances for applications in separation, catalysis, and sensors.[15] Besides, they can serve as ideal anchoring sites for guest species as well exemplified by the open Cr^{III} sites in MIL-101(Cr).[16] In principle, it is feasible to introduce CFLPs into MOFs by post-modification of open metal sites based on our previously developed strategy,[13] which, however, has been hindered by the lack of CFLPs involving bifunctional Lewis acid/Lewis base. To address such hindrance, herein we first employed computational calculations to examine the activities of a series of rationally designed CFLPs featuring bifunctional Lewis bases, which could be incorporated into MOF via step-wise anchoring approach.[13] In detail, *R*-piperazine, (1*R*,2*R*)-1,2-cyclohexanediamine, (1*R*,2*R*)-1,2-diphenyl-1,2-ethanediamine, and (*R*)-2,5-dihydro-3,6-dimethoxy-2-isopropylpyrazine were each coupled with tris(pentafluorophenyl)borane (BCF) as potential CFLPs, defining as CFLP1, CFLP2, CFLP3 and CFLP4, respectively (Figure 2).

In order to evaluate the possibility of H_2 activation with these CFLPs, the thermodynamic and kinetic Gibbs free energy were calculated following the equation $\Delta G = \Delta G([NH]^+[BH]^-) - \Delta G(N\cdots B) - \Delta G(H\text{–}H)$ at room temperature.[17] Meanwhile, the solvation corrected single-point energy calculations (based on the gas-phase optimized geometries) were also conducted to closely simulate the solvent effect of a real reaction using the M06 method in conjunction with the SMD solvation model3 in solvent (toluene). The obtained kinetic ΔG_{Ksol} value for CFLP1 to CFLP4 is 19.8, 22.1, 24.4 and 19.0 kcal mol^{-1}, respectively (Figure 2), indicative of the positive reaction rate. These values are comparable to the reported FLPs which can activate H_2.[18] The corresponding thermodynamic ΔG_{Tsol} value is −2.0, −1.5, −2.2, and −2.5 kcal mol^{-1}, respectively. Therefore, both kinetic and thermodynamic values suggest the feasibility of these rationally designed CFLPs for spontaneous H_2 activation with CFLP4 most active given its lowest calculated activation energies.[17,18]

In light of its framework robustness, large pore space, and high density of accessible open metal sites, MIL-101(Cr) was selected for the incorporation of the aforementioned CFLPs. Activation of MIL-101(Cr) released Cr^{III} open metal

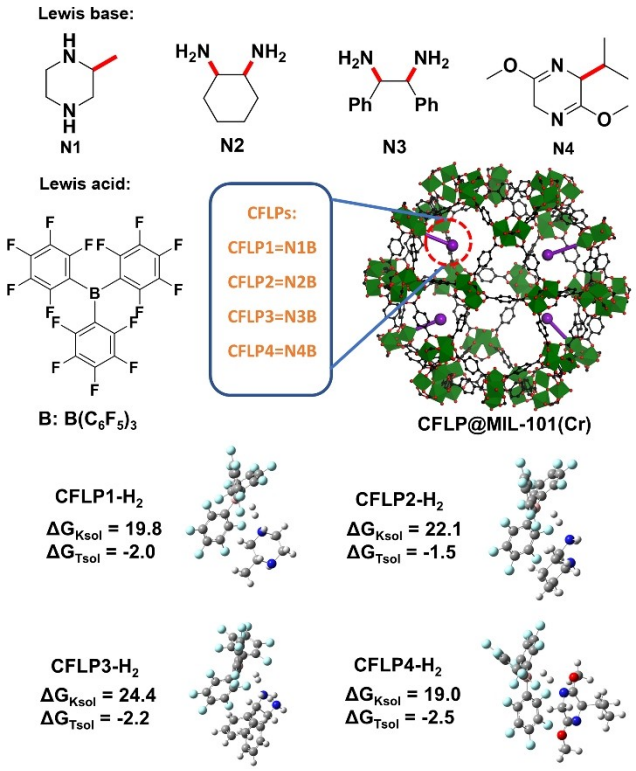


Figure 2. Computational screening of rationally designed bifunctional CFLPs for the activation of H_2.

sites after heating and degassing at 150 °C for 12 hours.[19] Subsequently, the target catalysts were prepared via anchoring different amounts of chiral bifunctional Lewis bases (the configuration is R unless otherwise stated) including 2-methylpiperazine, 1,2-cyclohexanediamine, 1,2-diphenyl-1,2-ethanediamine, and 2,5-dihydro-3,6-dimethoxy-2-isopropylpyrazine to the Cr^{III} open site with one N atom and then introducing equivalent amount of tris(pentafluorophenyl)borane to another N atom. The obtained catalysts were denoted as CFLPx-y@MIL-101(Cr), where x represents the category of CFLPs (number 1 to 4), and y indicates the loading amount of CFLPs (mmol g^{-1}).

Considering the lowest activation energies of CFLP4 among the four rationally designed CFLPs as suggested from computational calculations, our characterizations and catalysis studies were focused on CFLP4 and CFLP4-0.75@MIL-101(Cr). The framework integrity of the obtained catalyst remained unchanged as verified by the powder X-ray diffraction (PXRD) patterns of CFLPx-0.75@MIL-101(Cr) and MIL-101(Cr) (Figure S1, S2). N_2 sorption isotherms at 77 K revealed that, after the incorporation of CFLP4, the Brunauer–Emmett–Teller (BET) surface area decreased from 4032 $m^2 g^{-1}$ for MIL-101(Cr) to 2067 $m^2 g^{-1}$ for CFLP4-0.75@MIL-101(Cr), whereas the pore sizes of both samples are predominantly distributed in the range of 1.0–3.0 nm indicative of minimal pore blockage after CFLP introduction (Figure S3, S4). Meanwhile, the BET surface areas and pore size distributions of the other three CFLPx-0.75@MIL-101(Cr) samples were also examined, with results similar to CFLP4-0.75@MIL-101(Cr) (Figure S5–S7). The catalysts could be thermally stable up to 200 °C, with a weight loss corresponding to solvent evaporation as evident by thermogravimetric analysis (TGA) (Figure S8–S12). Additionally, elemental analysis confirmed the agreement between the measured and calculated contents of C, H, O, and N in CFLP4-0.75@MIL-101(Cr) (Table S1). Indeed, the existence of N in the sample suggested the successful introduction of the chiral pyrazine into MIL-101(Cr). Fourier transform infrared spectroscopy (FTIR) results (Figure S13–S16) showed that CFLP4-0.75@MIL-101(Cr) exhibited the characteristic peaks of both MIL-101(Cr) and CFLP4, proving the successful incorporation of CFLP4 into the MIL-101(Cr). Closer inspection of the C–H vibration signal revealed a shift in CFLP4-0.75@MIL-101(Cr) as compared with CFLP4 at around 3000 cm^{-1}, consistent with the formation of FLPs.[13a] The X-ray photoelectron spectroscopy (XPS) results also showed a new signal of N, B, and F in CFLP4-0.75@MIL-101(Cr) as compared with MIL-101(Cr) (Figure S17), further proving the successful incorporation of CFLP4 into MOF. In addition, CFLP4-0.75@MIL-101(Cr) showed higher Cr2p3 bonding energy than MIL-101(Cr) with an entire shift of 0.6 eV (Figure S18), which can be attributed to the coordination of chiral pyrazine to the open Cr sites.[13] Scanning electronic microscope (SEM) and transmission electronic microscope (TEM) revealed the octahedral morphology of CFLP4-0.75@MIL-101(Cr) with particle size of ≈100 nm (Figure 3). The energy dispersive spectrometer (EDS) elemental mapping clearly shows the presence of Cr, C, N, B, and F, indicating the existence and

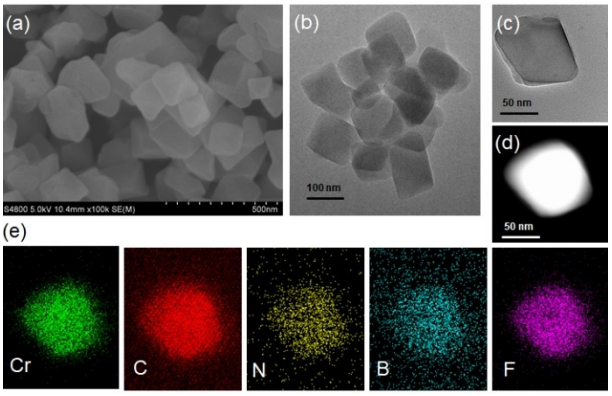


Figure 3. SEM image (a), TEM image (b and c), HAADF-STEM image (d), and elemental mapping image (e) of CFLP4-0.75@MIL-101(Cr).

uniform distribution of CFLP4 entities within CFLP4-0.75@MIL-101(Cr). Circular dichroism (CD) spectroscopy was employed to study the optical property of chiral amines (N1-N4), and reversal curves of R and S enantiomers (Figure S19–S22) were observed by measuring their methanol solutions. The optical activity of the solid samples was examined by vibrational circular dichroism (VCD). The prepared CFLP4-0.75@MIL-101(Cr) (both R and S) displayed reversal signals in the range of 2800–3000 cm^{-1} (Figure 4) as a result of the C–H stretching vibration as well as different interaction with circularly polarized light, suggesting the successful introduction of enantiomeric-pure chiral FLP molecules into MOF.

The catalysis performances of the obtained catalysts were examined in the context of asymmetric hydrogenation of imines with the isolated yields and enantiomeric excess (ee) values summarized in Table 1 and Table 2.

In the absence of CFLPs, MIL-101(Cr) itself could not drive the reaction for asymmetric hydrogenation of imine; in contrast, both CFLP4 and CFLP4-0.75@MIL-101(Cr) exhibited high catalytic activities (Table 1 Entry 1–3). Besides circumventing the difficulty in separating the products from the reaction mixtures as encountered for homogeneous catalysts, CFLP4-0.75@MIL-101(Cr) demonstrates notably higher catalysis performance with 95 % yield and 85 % ee value (Table 1 Entry 2) than the molecular CFLP4 catalyst (85 % yield and 80 % ee value) (Table 1 Entry 3), which can be presumably ascribed to the enriched concentration of

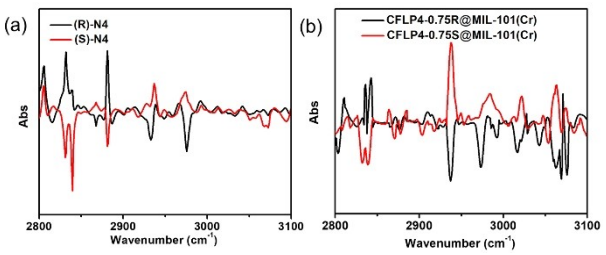
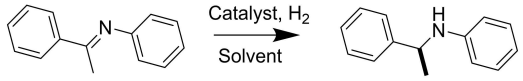


Figure 4. VCD spectra of chiral N4 (2,5-dihydro-3,6-dimethoxy-2-isopropylpyrazine) (a) and CFLP4-0.75@MIL-101(Cr) (b).

Table 1: Asymmetric hydrogenation catalyzed by various catalysts.



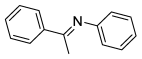
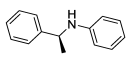
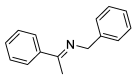
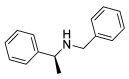
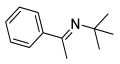
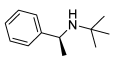
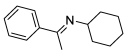
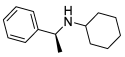
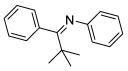
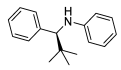
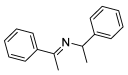
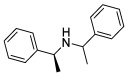
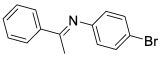
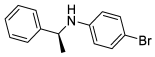
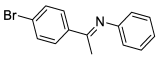
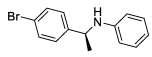
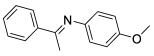
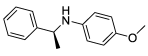
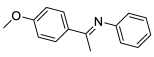
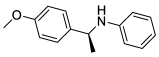
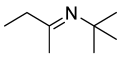
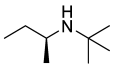
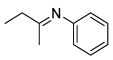
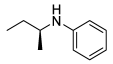
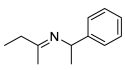
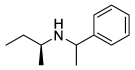
Entry	Catalyst	Solvent	Yield (%, ±1)	ee value (%, ±0.5)
1[a]	MIL-101(Cr)	Toluene	0	0
2	CFLP4-0.75@MIL-101(Cr)	Toluene	95	85
3	CFLP4	Toluene	85	80
4	CFLP4 + MIL-101(Cr)	Toluene	87	79
5[b]	CFLP4-0.75@MIL-101(Cr)	Toluene	97	86
6	CFLP4-0.5@MIL-101(Cr)	Toluene	85	78
7	CFLP4-1.0@MIL-101(Cr)	Toluene	96	65
8	CFLP4-0.75@MIL-101(Cr)	CH_2Cl_2	55	43
9	CFLP4-0.75@MIL-101(Cr)	CH_3CN	98	55
10	CFLP1-0.75@MIL-101(Cr)	Toluene	84	63
11	CFLP2-0.75@MIL-101(Cr)	Toluene	75	56
12	CFLP3-0.75@MIL-101(Cr)	Toluene	88	78

[a] Unless otherwise stated, the reaction proceeds under below conditions: 3 mL dry solvent, 20 mg catalyst, 0.2 mmol substrate, and 20 bar H_2, 48 hours at room temperature. Yield is determined by the weight of isolated product, and ee value is determined by HPLC. [b] CFLP4-0.75@MIL-101(Cr) of S configuration.

CFLP and the enforced stronger chiral environment within the nanospace of MOF.[4b–g,13] Mechanically mixing CFLP4 and MIL-101(Cr) afforded catalysis performance comparable to the molecular CFLP4 catalyst (Table 1 Entry 4), highlighting the role of MOF in promoting the catalysis. It's worth noting that, when the bulky substrate with diameter ($\approx$1.4 nm) larger than the window size of MIL-101(Cr) ($\approx$1.0 nm) was used, no detectable yield was observed for CFLP4-0.75@MIL-101(Cr) whereas considerable yield was obtained for the molecular CFLP4 catalyst (Table S2), suggesting that the catalysis occurs within the pore of CFLP4-0.75@MIL-101(Cr). Furthermore, no noticeable change in conversion ratio was observed after the filtration of solid catalysts during the reaction process while continually monitoring the reaction under otherwise unchanged conditions (Figure S23), proving that the hydrogenation was catalyzed by the heterogeneous catalyst and the CFLP leaching was negligible.[20]

Comparable catalysis performance was observed when the same amount of CFLP4 with S configuration was loaded into MIL-101(Cr) (Table 1 Entry 5). The effect of loading amounts of CFLPs on the catalysis performances of CFLP4@MIL-101(Cr) was investigated with 0.75 mmol g^{-1} as the optimal loading amount (Entry 5, 6 in Table 1). Lowering the CFLP4 loading amount to 0.5 mmol g^{-1} led to a decrease in catalysis performance (Table 1 Entry 6) due to the reduced number of active CFLP4 in MOF; increasing the CFLP loading amount to 1.0 mmol g^{-1} did not afford significant improvement in yield but resulted in substantial decline in ee value (Table 1 Entry 7), which could be presumably due to that the more crowded pore environment as a result of the increased number of CFLP4 sacrifices the needed free space for adjusting the optimal configuration of product thereby leading to lower stereoselectivity.

Table 2: Catalytic performance of CFLP4-0.75@MIL-101(Cr) toward asymmetric hydrogenation with different imines.

Entry	Substrate	Product	Yield (%, ±1)	ee value (%, ±0.5)
1			95	85
2			96	79
3			95	81
4			96	80
5			97	77
6			96	78
7			94	80
8			95	80
9			96	85
10			94	84
11			92	85
12			94	88
13			93	78

The reactions are carried out under below conditions: 3 mL dry toluene, 20 mg CFLP4-0.75@MIL-101(Cr), 0.2 mmol substrate, and 20 bar H_2, 48 hours at room temperature. Yield is determined by the weight of isolated product, and ee value is determined by HPLC.

We also assessed the solvent influence on catalysis performances of CFLP4@MIL-101(Cr), which revealed that toluene is the best to achieve both high yield and ee value among all tested solvents (toluene, CH_2Cl_2, CH_3CN). Much lower yield (55 %) and ee value (43 %) were observed when CH_2Cl_2 was used owing to the poor solubility of the substrates (Table 1 Entry 8). Although comparable yield (98 %) was achieved when the polar solvent of CH_3CN was used, lower ee value (55 %) was obtained (Table 1 Entry 9) because CH_3CN can facilitate the formation of achiral FLPs with BCF.[21] CFLP4-0.75@MIL-101(Cr) can be readily recycled and regenerated. No significant decrease in catalysis performance after five cycles (Figure S24), and CFLP4-0.75@MIL-101(Cr) also retained its structural intactness and porosity after catalysis as evident by the PXRD (Figure S25) and BET surface area measurements (Figure S26) verifying the heterogeneous nature of the catalyst.

The catalysis performances of MIL-101(Cr) loaded with other three rationally designed CFLPs were evaluated as well (Table 1 Entry 10–12). As expected, with the same

loading amount of CFLP (0.75 mmol g^{-1}), CFLP1-0.75@MIL-101(Cr), CFLP2-0.75@MIL-101(Cr) and CFLP3-0.75@MIL-101(Cr) exhibited poorer yields and lower ee values as compared with CFLP4-0.75@MIL-101(Cr), which correlated well with the computational calculation studies. These results suggested that the catalysis performance of CFLP@MIL-101(Cr) could be readily tuned by changing the type of CFLP and underscored the guiding role of computational studies on the rational design of molecular CFLP to construct highly active CFLP@MOF for heterogeneous asymmetric catalysis.

Bearing its superior catalysis performance in mind, we expanded the scope of substrates for asymmetric hydrogenation catalyzed by CFLP4-0.75@MIL-101(Cr) (Table 2). Hydrogenation of imines with different substitute groups on the N atom (phenyl-N, benzyl-N, tert-butyl-N, and cyclohexyl-N, respectively) led to quantitative yields (95 %, 96 %, 95 %, 96 %) and ee values (85 %, 79 %, 81 %, 80 %) (Table 2 Entry 1–4). Comparable yields and ee values were observed for substrates with steric hindrance at the C=N bond (Table 2 Entry 5 and 6); similar performances were also obtained for halogen substituted substrates (Table 2 Entry 7 and 8) and substrates with electron donating group ($-OCH_3$) (Table 2 Entry 9 and 10) were catalyzed to target products in good yields and ee values. Alkyl substituted substrates were catalytically converted into the corresponding products with good performance as well (Table 2 Entry 11–13). These results therefore highlight CFLP4-0.75@MIL-101(Cr) as an excellent catalyst for heterogeneous asymmetric hydrogenation of imines.

To gain some insights on the catalysis mechanism (Figure S27), solid-state ^{11}B nuclear magnetic resonance (NMR) spectra were measured for CFLP4-0.75@MIL-101(Cr)-H_2, CFLP4-0.75@MIL-101(Cr), and BCF, which showed the chemical shift of −20.5, −6.6 and 65.6, respectively (Figure 5) indicating the formation of CFLP and H_2 activation by CFLP in CFLP4-0.75@MIL-101(Cr).[22] In addition, the X-ray photoelectron spectroscopy (XPS) binding energy of B element in CFLP4-0.75@MIL-101(Cr)-H_2 exhibited an overall 0.5 eV shift compared with CFLP4-0.75@MIL-101(Cr) (Figure S28) because of an increase of electron density, implying the activation of H_2 via a heterolytic manner. These were consistent with the computational calculations, which suggested CFLP can activate H_2 with reasonable thermodynamic and kinetic Gibbs free energy. In particular, the atomic charge calculation of the CFLP4-H_2 transition state reflected the charge of B (−0.54927) and N (+0.56883), implying the heterolytic H_2 splitting by CFLP, which is in a good agreement with the mechanism of classic FLP for H_2 activation.[5] Furthermore, the chirality transfer from the chiral amine to the product proceeds under the assistance of hydrogen bonding,[23] in which the enantioselectivity is supported by the calculated energy difference (2.4 kcal mol^{-1}) between *R* and *S* isomer.

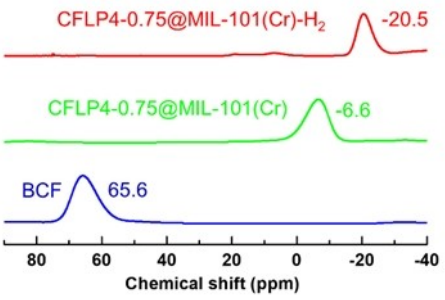


Figure 5. ^{11}B NMR spectrum of CFLP4-0.75@MIL-101(Cr)-H_2, CFLP4-0.75@MIL-101(Cr), and BCF (top to bottom).

Conclusion

In summary, under the guidance of computational studies on a series of rationally designed chiral frustrated Lewis pairs, a highly active CFLP@MOF system has been constructed for efficient heterogeneous asymmetric hydrogenation with excellent recyclability/regenerability. This work not only lays a solid foundation to develop CFLP@MOF as a new platform for heterogeneous asymmetric hydrogenation, but also suggests an approach by merging the frontiers of different chemistry fields to tackle some challenges in asymmetric catalysis and beyond.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Asymmetric Hydrogenation · Chiral · Frustrated Lewis Pair · Heterogeneous · Metal–Organic Framework

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