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DOI

[10.1021/jacs.9b05351](https://doi.org/10.1021/jacs.9b05351)

Publication date

2019

Document Version

Final published version

Published in

Journal of the American Chemical Society

License

Article 25fa Dutch Copyright Act

[Link to publication](#)

Citation for published version (APA):

Wei, J., Zhao, L., He, C., Zheng, S., Reek, J. N. H., & Duan, C. (2019). Metal-Organic Capsules with NADH Mimics as Switchable Selectivity Regulators for Photocatalytic Transfer Hydrogenation. *Journal of the American Chemical Society*, 141(32), 12707-12716. <https://doi.org/10.1021/jacs.9b05351>

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Metal–Organic Capsules with NADH Mimics as Switchable Selectivity Regulators for Photocatalytic Transfer Hydrogenation

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Supporting Information

ABSTRACT: Switchable selective hydrogenation among the groups in multifunctional compounds is challenging because selective hydrogenation is of great interest in the synthesis of fine chemicals and pharmaceuticals as a result of the importance of key intermediates. Herein, we report a new approach to highly selectively (>99%) reducing C=X (X = O, N) over the thermodynamically more favorable nitro groups locating the substrate in a metal–organic capsule containing NADH active sites. Within the capsule, the NADH active sites reduce the double bonds via a typical $2e^-$ hydride transfer hydrogenation, and the formed excited-state NAD^+ mimics oxidize the reductant via two consecutive $1e^-$ processes to regenerate the NADH active sites under illumination. Outside the capsule, nitro groups are highly selectively reduced through a typical $1e^-$ hydrogenation. By combining photoinduced $1e^-$ transfer regeneration outside the cage, both $1e^-$ and $2e^-$ hydrogenation can be switched controllably by varying the concentrations of the substrates and the redox potential of electron donors. This promising alternative approach, which could proceed under mild reaction conditions and use easy-to-handle hydrogen donors with enhanced high selectivity toward different groups, is based on the localization and differentiation of the $2e^-$ and $1e^-$ hydrogenation pathways inside and outside the capsules, provides a deep comprehension of photocatalytic microscopic reaction processes, and will allow the design and optimization of catalysts. We demonstrate the advantage of this method over typical hydrogenation that involves specific activation via well-modified catalytic sites and present results on the high, well-controlled, and switchable selectivity for the hydrogenation of a variety of substituted and bifunctional aldehydes, ketones, and imines.

INTRODUCTION

Transfer hydrogenation reactions that proceed under mild reaction conditions with easy-to-handle hydrogen donors instead of hydrogen gas are a rapidly growing field because they facilitate the practical synthesis of fine chemicals using complicated compounds with multiple functional groups.^{1–4} Recent breakthroughs in transfer hydrogenation have enabled the selective transformations of ketones^{5,6} and aldehydes^{7,8} into their corresponding alcohols in the presence of other functional groups, including thermodynamically more favorable hydrogenation groups such as nitroarenes and olefins. However, the direct activation of specific groups using well-modified catalytic sites precludes practically inverting and switching the selectivity of the hydrogenation in bifunctional compounds in a single catalytic process. A strategy for selective hydrogenation was proposed, which involves the differentiation of $2e^-$ (hydride) and $1e^-$ hydrogenation pathways. The hydride $2e^-$ transfer hydrogenation of ketones and aldehydes over substrates typically hydrogenated via $1e^-$ transfer pathways.⁹ Of particular interest is the $2e^-$ hydride transfer hydrogenation using redox cofactor NADH (reduced nicotinamide adenine nucleotide) and its mimics¹⁰ based on

its central role as a cosubstrate in biosynthetic pathways and the potential of NADH to serve as a hydride source while being a weak single-electron reductant.^{11,12} Therefore, new synthetic platforms in which the selectivity in the transformations of bifunctional compounds could be strictly controlled and readily tuned by regulating the reaction kinetics of the hydrogenation pathways involving NADH, such as those involving natural enzymes, may facilitate the selective preparation of fine chemicals and pharmaceuticals bearing multiple functional groups.

To mimic the remarkable abilities of enzymes to achieve efficient chemical conversions, researchers have used various molecular capsules, including symmetric metal–organic capsules with defined hydrophobic cavities that are spontaneously generated through preorganized ligands and functionalized metallocorners, as promising hosts to catalyze unique chemical transformations.^{13–16} Reactions performed in such molecular capsules could be enhanced by proximity effects allowing unusual selectivity and unique dynamics owing to the

Received: May 19, 2019

Published: July 18, 2019

restricted motion of the substrates. Recently, it was demonstrated that capsules can be used to separate redox events, exploiting the difference between the inner and outer spaces of a host to combine photocatalytic proton reduction and substrate oxidation in a one-pot transformation.^{17,18} Artificial enzymatic systems that combine photocatalytic chemical transformations, including proton reduction, to regenerate the active sites in NADH mimics and biomimetic hydrogenation reactions have also been postulated as a new synthetic platform.^{19–21} The localization of a $2e^-$ hydride transfer hydrogenation pathway inside the reaction vessel containing the NADH mimics thus allows the design and optimization of catalysts, which could proceed under mild reaction conditions and use easy-to-handle hydrogen donors with enhanced high selectivity.

We herein report a molecular flask with NADH-type cofactors that allows us to control the selectivity of a photocatalytic transfer hydrogenation reaction, toggling between a carbonyl or nitro group reduction in bifunctionalized compounds under mild reaction conditions (Scheme 1).

Scheme 1. Schematic of Switching the Transfer Hydrogenation Selectivity inside and outside the Pocket of the Capsule^a

^a*PS represents the excited-state photosensitizer.

Substrate binding in the molecular flask results in preorganization and thus facilitates typical $2e^-$ hydride transfer hydrogenation, which is highly selective for the carbonyl, whereas the $1e^-$ transfer hydrogenation events takes place when the substrate is outside the molecular flask. We envisioned that with this approach, aldehyde and ketone groups could be highly selectively hydrogenated in the presence of nitro groups that are thermodynamically more favorable to convert. These active NADH mimics could be regenerated from the formed NAD^+ mimics via oxidation of the reductant through two consecutive $1e^-$ reduction processes under illumination. Outside the pocket, a typical $1e^-$ transfer hydrogenation environment was modified by the presence of a reductant or photosensitizer to highly selectively reduce the nitro group over the carbonyl group. Notably, both hydrogenation processes are well controlled by strictly limiting the different electron transfer pathways to inside and outside the molecular host. The selectivity of the hydrogenation of bifunctional compounds could be inverted by simply regulating the reaction kinetics of the two hydrogenation pathways (i.e., varying the concentrations of the substrate and electron donor) because the kinetics inside the pocket are controlled only by the concentration of the host–guest complex and not directly by the concentration of the substrate.

RESULTS AND DISCUSSION

Preparation and Characterization of Macrocycles and the Host–Guest Complex. Ligand H_2FPB was synthesized by a Schiff-base reaction of 2-pyridylaldehyde and 1-(furan-2-ylmethyl)-4-phenyl-1,4-dihydropyridine-3,5-dicarbohydrazide in an ethanol solution. The M_4L_4 metal–organic macrocycles were prepared by reacting ligand H_2FPB with the appropriate metal salts in acetonitrile solution. Diffraction-grade single crystals of the macrocycles including Zn–FPB, Fe–FPB, Co–FPB, and Ni–FPB were obtained by the vapor diffusion of diethyl ether into the corresponding CH_3CN solutions of the macrocycles (Figures 1a,b and S1–S4).

Figure 1. Crystal structures of macrocycle Zn–FPB (a) with NADH-mimicking ligands showing the coordination geometry of the zinc ions and top view (b) of the macrocycle showing the resulting confined space. Crystal structures of host–guest complex Zn–FPB $\supset$ 1 (c) and macrocycle Ni–FMB (d) without NADH-mimicking ligands. Anions and solvent molecules are omitted for clarity. Zn, cyan; Ni, green; O, red; N, blue; C, gray; and H, white.

Single-crystal structure analyses revealed that the four macrocycles are isostructural and exhibit S_4 symmetry via the connection of four ligands with the dihydropyridine amido (DHPA) fragments and four metal ions in an alternating fashion.²² The four DHPA moieties are positioned on parallel edges of the molecular square with the phenyl ring outside of the cavity and the four active H atoms in the pocket interior.²³ Given the van der Waals radii (3.6 Å) of the guest molecules and the edges of the square, the average Zn···Zn separation of approximately 8.62 Å suggests that the cavity of the square is sufficiently large to encapsulate a planar aromatic substrate. Each zinc ion was coordinated in a mer position with a pair of extensively delocalized N_2O chelators to ensure the mobility of electrons along the whole backbone of the ligands. Such electrons have the potential to migrate from the metal centers to the active sites of the NAD^+ models, enabling the regeneration of the active sites from the photoreduced redox reaction involving the metal ions. The four furan rings are positioned above and below the molecular square to form a pocket for guest inclusion. Importantly, host–guest complex Zn–FPB $\supset$ 1 (4-nitrobenzaldehyde) was obtained by the same method, which provided unambiguous evidence for complex formation (Figures 1c and S5). Single-crystal structure analysis shows that one guest molecule, 1, binds in the pocket.²⁴ The main structure of the molecular square is maintained with the furan rings twisting in the lateral direction. The shortest

interatomic distance between **1** and the host structure is 3.52 Å.²⁵ Moreover, the molecule structures of both Zn–FPB and host–guest complex Zn–FPB ⊃ **1** determined from DFT calculation were consistent with their single-crystal structures (Figure S19).²⁶ There is close proximity between the active hydrides of the host and **1**, providing the possibility to stabilize the structurally confined intermediate for potential size- and shape-selective hydrogenation.²⁷

The structural stability of Zn–FPB in solution was further characterized by ESI–MS spectra that exhibited two sharp peaks at m/z = 793.83 and 1190.23 with the exact distribution fingerprint of the $[\text{H}_3\text{Zn}_4(\text{FPB})_4]^{3+}$ and $[\text{H}_2\text{Zn}_4(\text{FPB})_4]^{2+}$ species, respectively (Figure 2a). Guest binding in the pocket

Figure 2. ESI–MS spectra of Zn–FPB (a), Zn–FPB (b) following the addition of 5 equiv of substrate **1**, and Zn–FPB (c) following the addition of 5 equiv of inhibitor ATP in CH_3CN . The insets show the measured and simulated isotopic patterns at m/z = 793.83, 844.16, 1190.23, 1265.73, and 1444.74.

of the host is evident by ESI–MS analysis of a mixture of molecular macrocycle Zn–FPB and **1** that shows the appearance of two new peaks that correspond to the $[\text{H}_3\text{Zn}_4(\text{FPB})_4(\textbf{1})]^{3+}$ and $[\text{H}_2\text{Zn}_4(\text{FPB})_4(\textbf{1})]^{2+}$ species at m/z = 844.16 and 1265.73, respectively. A comparison of the experimental peaks with that obtained via simulation based on natural isotopic abundances suggested the formation of a 1:1 stoichiometric species, Zn–FPB ⊃ **1**, in solution (Figure 2b).

Further characterization of the host–guest complex comes from isothermal titration calorimetry (ITC) experiments, of which the spectrum fit well to a 1:1 binding model, providing both the enthalpy (ΔH = 0.03) and entropy ($T\Delta S$ = 24.83 kJ·mol^{−1}) of formation of complex Zn–FPB ⊃ **1** with association constant $2.21 \times 10^4 \text{ M}^{-1}$ (Figures 3a and S11).²⁸ The formation of the host–guest complex is also evident from the fluorescence titration (Figure S21) and the change in chemical shifts in the ¹H NMR spectra of both the substrate and molecular square (Figure S14). In addition, NOE contacts between the benzene rings of **1** and the NADH mimics of the molecular macrocycle were observed in the NOESY spectrum of the host–guest complex Zn–FPB ⊃ **1** (Figure S15), which suggests that **1** is in close contact with the host when bound in the macrocycle.²⁹ These results indicate that the formation of the host–guest complex was preorganized for efficient substrate activation.^{30,31}

Highly Selective Photocatalytic Transfer Hydrogenation. The activity of macrocycle catalyst Zn–FPB was first studied by chemical reduction of the different types of double

Figure 3. (a) ITC experiments on Zn–FPB upon the addition of substrate **1** or ATP showing the formation of host–guest complexes in CH_3CN . (b) Yields of (cyan bars) 4-nitrophenyl methanol (**1a**) and 4-aminobenzaldehyde (**1b**) by the system containing substrate **1** (5.0 mM), Zn–FPB (0.1 mM), NaBH_3CN (1.0 mM), and $\text{HCOOH}/\text{Et}_3\text{N}$ (0.1 M/0.05 M) in a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution (1:1, pH 8.50) for 6 h under 420 nm. The magenta, yellow, and gray bars show the yields of **1a** and **1b** in the presence of ATP (25.0 mM, yellow bars), benzoquinone (5.0 mM, magenta bars), and TEMPO (5.0 mM, gray bars).

bonds (carbonyl, imine, olefin, and nitro). The substrates containing double bonds $\text{C}=\text{N}$ and $\text{C}=\text{O}$ can be stoichiometrically reduced by Zn–FPB through the $2e^-$ hydride transfer hydrogenation in the presence of NaBH_3CN ³² and yield increases with the increase in substrate potential (Table 1). In the presence of an electron-withdrawing group, the conversion of the transfer hydrogenation significantly increased, whereas an electron-donating group significantly decreased the benzaldehyde conversion. However, neither an electron-withdrawing nor electron-donating group changed the reactivity of nitrobenzene as it stayed inert for the $2e^-$ transfer hydrogenation, even though the reduction of the nitro group is thermodynamically more favorable than the reduction of the carbonyl group.

In the model reaction of substrate **1** (5.0 mM) containing both nitro and aldehyde groups, Zn–FPB stoichiometrically yielded product **1a** (4-nitrophenylmethanol, 91%) with over 99% selectivity. Localizing the electron donors (i.e., $\text{HCOOH}/\text{Et}_3\text{N}$) outside the capsules to in situ regenerate the active sites of the NADH mimics^{33,34} allowed Zn–FPB to operate as an efficient catalyst and achieve highly selective hydrogenation under light illumination. While the ground-state NAD^+ mimic is a weak single-electron oxidant, the excited-state NAD^+ mimic is a strong oxidant that is able to extract two electrons consecutively from the reductant in the solution, quickly regenerating the active NADH mimic. The loading of Zn–FPB (0.1 mM) resulted in 82% conversion of **1a** with a selectivity of 98% after 6 h under 420 nm LED light illumination, and the conversion of thermodynamically favored hydrogenation product **1b** (4-aminobenzaldehyde) is less than 1% (Figure 3b). The results indicate that our approach of localizing the NADH-cofactor-derived biomimetic $2e^-$ hydride transfer hydrogenation pathway to control the selectivity is feasible.

Control experiments using the related salts and ligands yielded a trace of the product under the same conditions, confirming that the supermolecular host used to preorganize the substrate is essential. When the concentrations of $\text{HCOOH}/\text{Et}_3\text{N}$ and **1** are fixed, the initial rate constant for hydrogenation exhibited a linear relationship with the concentration of Zn–FPB (Figure 4a). When the concentrations of **1** and Zn–FPB are fixed, the initial turnover frequency of hydrogenation did not vary with the concentration of $\text{HCOOH}/\text{Et}_3\text{N}$, but the conversion of **1** increased

Table 1. Evaluation of Hydrogenation for Different Types of Unsaturated Groups and Unsaturated Groups Containing Electronic Pushing and Drawing Substituents with Zn-FPB^a

No.	Substrates	Potential (eV)	Yield (%)	No.	Substrates	Potential (eV)	Yield (%)	No.	Substrates	Potential (eV)	Yield (%)
2		-1.31	Trace	7		-1.29	87	12		-1.06	Trace
3		-1.42	86	8		-1.61	75	13		-1.19	Trace
4		-1.68	47	9		-1.66	57	14		-1.36	Trace
5		-1.75	36	10		-1.79	26	15		-1.46	Trace
6		-2.62	Trace	11		-1.88	28	16		-1.49	Trace

^aReaction conditions: Substrate (10.0 mM), Zn-FPB (10.0 mM), and NaBH₃CN (10.0 mM) in CH₃CN/H₂O solution (1:1, 5 mL), 6 h. The conversions were determined by ¹H NMR spectroscopy of the crude products. The redox potentials of substrates were determined by cyclic voltammetry of the 1.0 mM CH₃CN/H₂O solution containing 0.1 M KCl. Scan rate: 100 mV/s.

Figure 4. Kinetics of the hydrogenation reaction by the system containing (a) substrate **1** (5.0 mM), HCOOH/Et₃N (0.1/0.05 M) and NaBH₃CN (1.0 mM) with different concentrations of Zn-FPB and (b) substrate **1** (5.0 mM), Zn-FPB (0.1 mM), and NaBH₃CN (1.0 mM) with different concentrations of HCOOH/Et₃N in a CH₃CN/H₂O solution (1:1, pH 8.50) under 420 nm illumination.

(Figure 4b). The dependence of the reaction rate on the host-guest concentration of the Zn-FPB ⊃ **1** species rather than the concentration of **1** or the electron donor is in line with a mechanism in which the reaction occurs within the pocket of Zn-FPB (Figure S16).³⁵ In line with this, the use of a substrate with bulky substituent **17** (3,5-bis(4-nitrophenyl)-benzaldehyde), which is too large to fit in the cavity of Zn-FPB, yielded only 17% of the desired product under the same conditions.

We wondered if we could also switch the catalyst properties by binding a competing guest in the host.³⁶ Adenosine triphosphate (ATP) has a width similar to that of **1**, which is smaller than the inner space of the pocket in Zn-FPB. Importantly, two negative charges and multiple hydrogen bonding sites endow ATP with larger binding constants than that of neutral substrates for positively charged Zn-FPB, and ATP that is inactive toward hydrogenation was usually chosen as a competitive guest introduced into the system.³⁷ The ITC result shows a 1:1 encapsulation of ATP within the pocket of Zn-FPB (Figures 3a and S12) with ΔH (1.76 kJ·mol⁻¹), $T\Delta S$ (31.4 kJ·mol⁻¹), and the association constant (1.58×10^5 M⁻¹).²⁸ This result was further determined by fluorescence titration (Figure S22), which had a higher affinity for the host than **1** had. Moreover, ITC titration was further tested by the addition of ATP to a solution of the complex of Zn-FPB and

1 (1:1) and was well fit using a “competitive replacement” model (Figure S13),^{38,39} providing association constants of 3.07×10^4 and 1.59×10^5 M⁻¹ with **1** and ATP, respectively, which was consistent with previous data. The results further confirmed that ATP was a good competitive guest for encapsulating into the cavity of Zn-FPB to replace substrate **1**. Upon the addition of ATP (25.0 mM) to the aforementioned catalytic system, the yield of complex Zn-FPB ⊃ ATP was over 90% ($K_{ATP}[ATP] > 25K_{sub}[sub]$) under the reaction conditions. Indeed, a catalysis experiment using **1** as a substrate in the presence of ATP (25.0 mM) caused a significant decrease in the yield of **1a** (82%, cf. 26%) compared to the yield in the absence of ATP (Figure 3b). This shows that ATP effectively competes with **1** for binding in the pocket, and as such, the catalyst properties can be controlled by using this as a cofactor.⁴⁰

From a mechanistic viewpoint, the encapsulation of a substrate in a pocket forces the active sites to be in close proximity to the substrate, enabling efficient hydrogenation in the pocket and gave the oxidation state of the active sites (NAD⁺ mimics) (Figure S23).⁴¹ Under illumination, the oxidation state NAD⁺ mimics were regenerated via photo-induced electron transfer from electron donors outside the flask (Figures 5 and S18).^{37,42} DFT calculations were further performed to determine the molar free-energy changes of the 2e⁻ hydride transfer hydrogenation and 1e⁻ transfer hydrogenation processes for the hydride donors and reaction intermediates, respectively. The molar free energy of Zn-FPB was 54.72 kcal·mol⁻¹ through a 2e⁻ hydride transfer hydrogenation process, which is 20.08 kcal·mol⁻¹ lower than that of the 1e⁻ transfer process, ensuring efficient hydrogenation of the Zn-FPB system through a 2e⁻ hydride transfer hydrogenation (Figure S20). The energy was also 8.48 kcal·mol⁻¹ lower than that of Ph-HEH, indicating that the 2e⁻ hydride transfer hydrogenation of the flask is more favorable than that of Ph-HEH.⁴³ Control experiments in the presence of benzoquinone⁴⁴ or TEMPO⁴⁵ as radical scavengers caused a significant decrease in the conversion of **1a**, reaching 14 and 18%, respectively (Figure 3b). The result confirmed that the photoinduced electron transfer (PET) processes relevant to the excited state of the NAD⁺ mimics are dominant in the in

Inside the pocket: Hydride ($2e^-$) Transfer Hydrogenation Outside the pocket: Typical $1e^-$ Transfer Hydrogenation

Figure 5. Schematic picture of transfer hydrogenation reactions taking place inside the host and outside, leading to different chemoselectivity. When the substrate is in the pocket, the $2e^-$ hydride transfer hydrogenation reaction with the NADH cofactor of the molecular host results in carbonyl reduction, whereas the reaction outside the active host results in nitro reduction via $1e^-$ transfer events.

situ regeneration of the NADH mimic active sites.⁴⁶ The superiority of such combined systems that promote the highly selective hydrogenation reaction by controlling the electron-transfer pathway using clean energy could be extended to several types of different functional groups (Table 2, 18a–28a). This selective hydrogenation reaction system was not only available for the aromatic compounds but also had better catalytic activity with respect to the aliphatic compounds containing alkyl or alkenyl groups (29a–32a). Simultaneously, the different types of alkenyl groups did not affect the selective catalytic hydrogenation (33a–36a).

The widespread demand of the flavoring, perfume, and pharmaceutical industries for unsaturated alcohols, which are key intermediates in the preparation of cinnarizine, flunarizine, and naftifine,^{47,48} is met by producing these alcohols from α,β -unsaturated aldehydes via highly selective hydrogenation of the carbonyl group. Benzhydrylpiperazine or 1-naphthalenemethanamine were added to the aforementioned reaction system to directly prepare drug molecules by a one-pot synthesis. Under typical conditions, benzhydrylpiperazine and 1-naphthalenemethanamine (12.0 mM), Zn-FPB (0.2 mM), and cinnamaldehyde (4.0 mM) yielded 71 and 55% cinnarizine and naftifine with 94 and 97% selectivities, respectively, in 12 h under 420 nm LED light illumination (Table 3).

Switchable Selectivity of Photocatalytic Transfer Hydrogenation. While changing the redox potential of the electron donors changed the product conversion, the hydrogenation selectivity could not be influenced, except in the presence of $\text{Na}_2\text{S}_2\text{O}_4$ (Figure 6a). The highly negative potential of $\text{Na}_2\text{S}_2\text{O}_4$ reduced the nitro group outside the pocket to give 1b while simultaneously donating electrons to the NAD^+ mimics to in situ regenerate the active sites for hydrogenation of the aldehyde group.^{49,50} Clearly, the modification of the electron-donating ability can tune the selectivity of hydrogenation toward 1a and 1b.

$\text{Ir}(\text{ppy})_2(\text{phen})^+$ is a well-known photosensitizer that drives several photocatalytic reactions⁵¹ and exhibits a similar absorption band⁵² compared to that of the NAD^+ mimics with a negative redox potential in its reduced state, $\text{Ir}(\text{ppy})_2(\text{phen})$. The luminescent titration of $\text{Ir}(\text{ppy})_2(\text{phen})^+$

Table 2. Evaluation of the Scope in Hydrogenation Catalysis along with the Highly Selective Hydrogenation of Different Types of Substrates with Functional Groups^a

$\text{O}_2\text{N}-\text{R}_1-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{R}_2 \xrightarrow[\text{CH}_3\text{CN}/\text{H}_2\text{O} (1:1), 420\text{nm LED}]{\text{Zn-FPB (2 mol\%)} \atop \text{NaBH}_3\text{CN (20 mol\%)} \atop \text{HCOOH}/\text{Et}_3\text{N} (0.1/0.05 \text{ M}), \text{rt, 6h}}$ $\text{O}_2\text{N}-\text{R}_1-\text{C}_6\text{H}_4-\text{CH}_2\text{OH}-\text{R}_2$			
1a: 82%(98%)	18a: 72%(95%)	19a: 55%(97%)	20a: 62%(97%)
21a: 64%(97%)	22a: 43%(95%)	23a: 61%(96%)	24a: 51%(96%)
$\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{R} \xrightarrow[\text{CH}_3\text{CN}/\text{H}_2\text{O} (1:1), 420\text{nm LED}]{\text{Zn-FPB (2 mol\%)} \atop \text{NaBH}_3\text{CN (20 mol\%)} \atop \text{HCOOH}/\text{Et}_3\text{N} (0.1/0.05 \text{ M}), \text{rt, 6h}}$ $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2\text{NH}-\text{R}$			
25a: 91%(94%)	26a: 92%(95%)	27a: 84%(92%)	28a: 88%(92%)
$\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{R}_2 \xrightarrow[\text{CH}_3\text{CN}/\text{H}_2\text{O} (1:1), 420\text{nm LED}]{\text{Zn-FPB (2 mol\%)} \atop \text{NaBH}_3\text{CN (20 mol\%)} \atop \text{HCOOH}/\text{Et}_3\text{N} (0.1/0.05 \text{ M}), \text{rt, 6h}}$ $\text{O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2\text{OH}-\text{R}_2$			
29a: 51%(93%)	30a: 36%(91%)	31a: 56%(96%)	32a: 67%(93%)
$\text{R}_2-\text{CH}=\text{CH}-\text{R}_1-\text{CHO} \xrightarrow[\text{CH}_3\text{CN}/\text{H}_2\text{O} (1:1), 420\text{nm LED}]{\text{Zn-FPB (2 mol\%)} \atop \text{NaBH}_3\text{CN (20 mol\%)} \atop \text{HCOOH}/\text{Et}_3\text{N} (0.1/0.05 \text{ M}), \text{rt, 6h}}$ $\text{R}_2-\text{CH}=\text{CH}-\text{R}_1-\text{CH}_2\text{OH}$			
33a: 78%(98%)	34a: 92%(99%)	35a: 90%(99%)	36a: 64%(97%)

^aReaction conditions: Substrate (5.0 mM), Zn-FPB (0.1 mM), $\text{HCOOH}/\text{Et}_3\text{N}$ (0.1 M/0.05 M), and NaBH_3CN (1.0 mM) in a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution (1:1, pH 8.50) for 6 h under 420 nm illumination. Yields were determined by ^1H NMR spectroscopy of crude products, and the selectivities are labeled in parentheses.

Table 3. Evaluation of the Scope of Hydrogenation Catalysis along with the Synthesis of Drug Molecules Cinnarizine and Naftifine^a

$\text{Cinnamaldehyde} + \text{R}_1\text{NH}-\text{R}_2 \xrightarrow[\text{CH}_3\text{CN}/\text{H}_2\text{O} (1:1), 420\text{nm LED}]{\text{Zn-FPB (5 mol\%)} \atop \text{NaBH}_3\text{CN (20 mol\%)} \atop \text{HCOOH}/\text{Et}_3\text{N} (0.1/0.05 \text{ M}), \text{rt, 12h}}$ Cinnarizine		37a (71%)
$\text{Cinnamaldehyde} + \text{R}_1\text{NH}-\text{R}_2 \xrightarrow[\text{CH}_3\text{CN}/\text{H}_2\text{O} (1:1), 420\text{nm LED}]{\text{Zn-FPB (5 mol\%)} \atop \text{NaBH}_3\text{CN (20 mol\%)} \atop \text{HCOOH}/\text{Et}_3\text{N} (0.1/0.05 \text{ M}), \text{rt, 12h}}$ Naftifine		38a (55%)

^aReaction conditions: Cinnamaldehyde (4.0 mM), Zn-FPB (0.2 mM), benzhydrylpiperazine or 1-naphthalenemethanamine (12.0 mM), $\text{HCOOH}/\text{Et}_3\text{N}$ (0.1 M/0.05 M), and NaBH_3CN (1.0 mM) in a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution (1:1, pH 8.50) for 12 h under 420 nm illumination. Yields were determined by ^1H NMR spectroscopy of crude products.

Figure 6. Switchable selectivity of the photocatalytic transfer hydrogenation: (a) Conversion of the hydrogenation by the system containing substrate **1** (5.0 mM), Zn-FPB (0.1 mM), and NaBH₃CN (1.0 mM) with different reducing agents (0.1 M). (b) Zn-FPB (0.1 mM), HCOOH/Et₃N (0.1/0.05 M), and NaBH₃CN (1.0 mM) with different reaction concentrations of substrate **1** (the total concentration is same) in a CH₃CN/H₂O solution (1:1, pH 8.50) under 420 nm illumination.

upon the addition of **1** and electron donors HCOOH/Et₃N and Zn-FPB at the same concentrations used in the reaction suggested that a photoinduced electron transfer from Ir(ppy)₂(phen)⁺ to **1** dominated the excited quenching processes (Figures S24–S27). The addition of Ir(ppy)₂(phen)⁺ (1.0 mM) in the aforementioned reaction mixture gave the major product as **1b** in 64% yield with a 22% yield of minor product **1a**. When decreasing the reaction

concentration of **1** (2.5 μmol/time, 10 times), the photo-induced electron transfer from electron donors HCOOH/Et₃N to Ir(ppy)₂(phen)⁺ dominated the excited quenching processes to give reduced Ir(ppy)₂(phen),⁵¹ which further reduced catalyst Zn-FPB and **1**.⁵³ The major product was **1b** in a decreased yield of 54%, and the yield of minor product **1a** increased to 33% (Figure 7a).

Ni-FPB (Figures 7c and S7) as a catalyst yielded 81% **1a** with a high selectivity greater than 99% in the presence of HCOOH/Et₃N as a reductant, and the addition of Ir(ppy)₂(phen)⁺ (1.0 mM) to the reaction mixture decreased the yield of **1a** to 18% with a **1b** yield of 70% (Table S14). We lowered the reaction concentration of **1** (2.5 μmol/time, 10 times) to decrease the quenching process of **1** on the photosensitizer (Figures S27 and S28) and the reaction rate outside the molecular flask, and reduced Ir(ppy)₂(phen) reduced the redox-active metal ions in the host, which further enhanced the regeneration of NADH mimics. The major product was switched to **1a** with a yield of 71% and a selectivity of more than 85% (Figure 6b) by the carefully regulation of the reaction kinetics inside and outside the host with respect to the influence of the thermodynamically favored hydrogenation groups. The results indicated that this simple approach to localizing and differentiating 2e[−] and 1e[−] hydrogenation pathways inside and outside the pocket could

Figure 7. Switchable selectivity of the photocatalytic transfer hydrogenation: Yields of (a) 4-nitrophenylmethanol (**1a**, red) and 4-aminobenzaldehyde (**1b**, blue) by the system containing substrate **1** (5.0 mM), catalysts (0.1 mM), HCOOH/Et₃N (0.1/0.05 M), NaBH₃CN (1.0 mM) and of (b) 1,2-bis(4-nitrophenyl)diazene (**39a**, red) and ursol (**39b**, blue) by the system containing substrate **39** (5.0 mM), catalysts (0.1 mM), HCOOH/Et₃N (0.1/0.05 M), and NaBH₃CN (1.0 mM) in a CH₃CN/H₂O solution (1:1, pH 8.50) under 420 nm illumination. Crystal structures of macrocycles (c) Ni-FPB, (d) Co-FPB, and (e) Fe-FPB with NADH-mimicking ligands. Anions and solvent molecules are omitted for clarity. Ni, green; Co, orange; Fe, violet; O, red; N, blue; C, gray; and H, white.

comfortably tune the selectivity of the two functional groups in bifunctional chemicals. Clearly, the selectivity of the hydrogenation product toward **1a** and **1b** can be directly switched via varying the substrate concentration (Figure S29). A control experiment based on molecular flask Ni-FMB (Figures 1d, S6, and S8) that resembles both the coordination geometry of the nickel(II) ion and the molecular square but with a central benzene ring replacing the center ring of the NADH mimics gave >80% selectivity of **1b** under the same conditions in the presence of Ir(ppy)₂(phen)⁺, even when lowering the reaction concentration of **1** (Figure S30 and Table S14). The absence of NADH mimics prevents any switchable possibility of selectivity. Such a switching approach could also be extended to the redox-active hosts containing Co(II) and Fe(II) ions (Figures 7d,e, S9, and S10). The differences in the selectivity for **1a** over **1b** even in the presence of a photosensitizer suggested that the electron-donating ability to the redox-active metal ions, in addition to the NAD⁺ mimics, is an important factor influencing the in situ regeneration of the active sites, the conversion, and the hydrogenation selectivity (Figures S31 and S32 and Table S14). A simple comparison of the selectivity of **1a** with the redox potentials of these molecular squares further confirmed that the direct electron transfer from the reduction state of the photosensitizer outside the pocket to the catalyst hosts dominates the in situ generation of the active sites (Figure S17).

39 (*p*-(nitroso)nitrobenzene), which contains two reducing groups with different electron transfer pathways, was selected as another typical substrate to demonstrate the broader applicability of the approach (Figure S33). Generally, the reduction of a nitro group to an amino group requires six electrons and six protons.⁵⁴ The reductions of a nitro group to a nitroso group and a hydroxylamine to an amino were through a 1e[−] transfer hydrogenation process, whereas the reduction of nitroso to hydroxylamine occurs through a 2e[−] hydride transfer hydrogenation.⁵⁵ In the absence of the photosensitizer, 1,2-bis(4-nitrophenyl)diazene (**39a**)⁵⁶ was obtained with a selectivity of >99% (Table S15). Substrate **39** (5.0 mM) was added to the solution containing Ir(ppy)₂(phen)⁺ (1.0 mM), and ursol (**39b**) was obtained in an 80% yield. By lowering the reaction concentration of **39** (2.5 μmol/time, 10 times), an 89% yield of **39a** with a 90% selectivity was achieved after 6 h (Figure 7b). Because **39a** was formed by mixing a nitroso group with hydroxylamine in solution, the switchable selectivity should be attributed to the selective reduction of the nitro group through a 1e[−] electron transfer process outside the flask, whereas the reduction of the nitroso group is through a 2e[−] hydride transfer hydrogenation inside the flask (Figures 8 and S34).

Figure 8. (a) Normalized fluorescence of Ir(ppy)₂(phen)⁺ (1.0 mM, black line) and of the aforementioned solution upon addition of **39** (0.5 mM, red line), **39** (5.0 mM, blue line), or HCOOH/Et₃N (0.1/0.05 M, green line). (b) Selective hydrogenation pathways of the *p*-(nitroso)nitrobenzene.

In summary, by incorporating NADH active sites into metal–organic hosts to localize the hydrogenation events inside and outside the pocket, we establish a new approach for modifying 2e[−] hydride transfer hydrogenation and 1e[−] transfer hydrogenation pathways to control and switch the selectivity between C=X (X = O, N) groups and nitro groups in bifunctional compounds. Inside the molecular flask, the NADH active sites highly selectively reduce the C=X (X = O, N) groups in the pocket via a typical 2e[−] hydride transfer hydrogenation, and the formed excited-state NAD⁺ mimics oxidize the reductant via two consecutive 1e[−] processes to regenerate the NADH active sites under illumination. Outside the molecular flask, electron donors in the ground state or in the excited state highly selectively reduce nitro groups through a typical 1e[−] hydrogenation process. Notably, the selectivity of hydrogenation of bifunctional compounds could be switched by simply regulating the reaction kinetics of the two hydrogenation pathways (i.e., by varying the concentrations of the substrate and electron donor) because the kinetics inside the pocket are controlled only by the concentration of the host–guest complex and not directly by the concentration of the substrate. Thus, this method represents a new synthetic platform for the designation of a novel photocatalysis. Compared to other reported transfer hydrogenation approaches, our approach of localizing the NADH-cofactor-derived biomimetic 2e[−] hydride transfer hydrogenation pathway inside a molecular flask to control the electron transfer pathway and the high selectivity of the product are quite significant, representing an unexplored intersection of group-selective syntheses, catalysis with earth-abundant metals, photoinduced processes, and transfer hydrogenation, each of which represents an important current theme in chemical synthesis.

EXPERIMENTAL SECTION

Synthesis of H₂FPB. Compound 1-(furan-2-ylmethyl)-4-phenyl-1,4-dihydropyridine-3,5-dicarbohydrazide (3.53 g, 10 mmol) was added to an ethanol solution (50 mL) containing 2-pyridylaldehyde (2.35 g, 22 mmol). After 5 drops of acetic acid was added, the mixture was held at 85 °C under magnetic stirring for 12 h according to the reference. The yellow solid was collected by filtration, washed with methanol, and dried in vacuum. Yield: 3.29 g, 65.6%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 11.38 (s, 2H), 8.57 (d, *J* = 4.4 Hz, 2H), 8.24 (s, 2H), 7.84 (m, 4H), 7.75 (s, 1H), 7.47 (s, 2H), 7.37 (m, 2H), 7.24 (m, 4H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.52 (s, 2H), 5.33 (s, 1H), 4.76 (s, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆, ppm): δ 163.9, 153.5, 150.6, 149.4, 146.4, 145.3, 143.5, 136.7, 135.2, 128.1, 127.6, 126.2, 124.0, 119.6, 110.7, 109.3, 108.8, 50.1, 36.1. Elemental analysis calcd for C₃₀H₂₅N₇O₃: H 4.74, C 67.79, N 18.44%. Found: H 4.82, C 67.01, N 18.21%. ESI-MS calcd for C₃₀H₂₅N₇O₃ 531.2019, found 532.2088 [M + H]⁺ (100%), 554.1927 [M + Na]⁺ (8%).

Synthesis of H₂FMB. Compound 5-(furan-2-ylmethyl)isophthalaldehyde (2.84 g, 10 mmol) was added to an ethanol solution (50 mL) containing 2-pyridylaldehyde (2.35 g, 22 mmol). After 5 drops of acetic acid was added, the mixture was held at 85 °C under magnetic stirring for 12 h according to the reference. The yellow solid was collected by filtration, washed with methanol, and dried in vacuum. Yield: 3.82 g, 83%. ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 12.24 (s, 2H), 8.64 (d, *J* = 4.4 Hz, 2H), 8.51 (s, 2H), 8.37 (s, 1H), 8.02 (m, 4H), 7.90 (t, *J* = 7.6 Hz, 2H), 7.58 (s, 1H), 7.44 (t, *J* = 6.4 Hz, 2H), 6.41 (s, 1H), 6.24 (s, 1H), 4.18 (s, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆, ppm): δ 162.7, 153.2, 153.1, 149.5, 148.5, 142.2, 139.4, 136.9, 133.8, 131.3, 125.1, 124.5, 120.0, 110.6, 106.8, 33.3. Elemental analysis calcd for C₂₅H₂₀N₆O₃: H 4.46, C 66.36, N 18.57%. Found: H 4.56, C 65.57, N 18.41%. ESI-MS calcd for C₂₅H₂₀N₆O₃ 452.1597, found 453.1681 [M + H]⁺ (100%), 475.1476 [M + Na]⁺ (9%).

Preparation of Zn–FPB. $\text{Zn}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (34.7 mg, 0.10 mmol) and H_2FPB (53.2 mg, 0.10 mmol) were dissolved in CH_3CN to give a yellow solution. The solution was diffused with ether for several days at room temperature to give X-ray-quality yellow block crystals. Yield: 68%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, ppm): δ 12.00 (s, 2H), 8.53 (s, 2H), 8.33 (s, 2H), 7.93 (m, 4H), 7.76 (s, 1H), 7.61 (s, 2H), 7.51 (s, 2H), 7.22 (m, 4H), 7.12 (m, 1H), 6.53 (s, 2H), 5.29 (s, 1H), 4.84 (s, 2H). Elemental analysis calcd for $\text{Zn}_4(\text{C}_{30}\text{H}_{24}\text{N}_7\text{O}_3)_4 \cdot 4\text{BF}_4 \cdot 2\text{CH}_3\text{CN}$: H 3.65, C 52.94, N 14.94%. Found: H 3.68, C 52.77, N 14.88%. ESI–MS: m/z : 793.8252 $[\text{H}_3\text{Zn}_4(\text{FPB})_4]^{3+}$ (100%), 1190.2319 $[\text{H}_2\text{Zn}_4(\text{FPB})_4]^{2+}$ (78%).

Preparation of Zn–FPB $\supset$ 1. $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (36.1 mg, 0.10 mmol), H_2FPB (53.2 mg, 0.10 mmol), and 4-nitrobenzaldehyde (37.8 mg, 0.25 mmol) were dissolved in CH_3CN to give a yellow solution. The solution was diffused with ether for several days at room temperature to give X-ray-quality yellow block crystals. Yield: 38%. Elemental analysis calcd for $\text{Zn}_4(\text{C}_{30}\text{H}_{25}\text{N}_7\text{O}_3)_4 \cdot 8\text{CF}_3\text{SO}_3 \cdot \text{C}_7\text{H}_5\text{NO}_3 \cdot 2\text{CH}_3\text{CN}$: H 2.93, C 43.78, N 11.39%. Found: H 2.95, C 43.69, N 11.37%. ESI–MS: m/z : 844.1558 $[\text{H}_3\text{Zn}_4(\text{FPB})_4 \supset (1)]^{3+}$ (25%), 1265.7304 $[\text{H}_2\text{Zn}_4(\text{FPB})_4 \supset (1)]^{2+}$ (24%).

Preparation of Fe–FPB. $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (36.3 mg, 0.10 mmol) and H_2FPB (53.2 mg, 0.10 mmol) were dissolved in CH_3CN to give a yellow solution. The solution was diffused with ether for several days at room temperature to give X-ray-quality purple block crystals. Yield: 54%. Elemental analysis calcd for $\text{Fe}_4(\text{C}_{30}\text{H}_{24.5}\text{N}_7\text{O}_3)_4 \cdot 6\text{ClO}_4 \cdot \text{CH}_3\text{CN}$: H 3.41, C 49.08, N 13.61%. Found: H 3.43, C 48.97, N 13.57%. ESI–MS: m/z : 785.5038 $[\text{H}_3\text{Fe}_4(\text{FPB})_4]^{3+}$ (69%), 1171.7513 $[\text{H}_2\text{Fe}_4(\text{FPB})_4]^{2+}$ (100%).

Preparation of Co–FPB. $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (34.0 mg, 0.10 mmol) and H_2FPB (53.2 mg, 0.10 mmol) were dissolved in CH_3CN to give a yellow solution. The solution was diffused with ether for several days at room temperature to give X-ray-quality red block crystals. Yield: 33%. Elemental analysis calcd for $\text{Co}_4(\text{C}_{30}\text{H}_{24}\text{N}_7\text{O}_3)_4 \cdot 4\text{BF}_4$: H 3.58, C 53.28, N 14.50%. Found: H 3.61, C 53.12, N 14.46%. ESI–MS: m/z : 785.4830 $[\text{H}_3\text{Co}_4(\text{FPB})_4]^{3+}$ (100%), 1177.6599 $[\text{H}_2\text{Co}_4(\text{FPB})_4]^{2+}$ (83%), 1231.2565 $[\text{H}_3\text{Co}_4(\text{FPB})_4 \cdot \text{BF}_4]^{2+}$ (40%).

Preparation of Ni–FPB. $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (36.5 mg, 0.10 mmol) and H_2FPB (54.2 mg, 0.10 mmol) were dissolved in CH_3CN to give a yellow solution. The solution was diffused with ether for several days at room temperature to give X-ray-quality yellow block crystals. Yield: 56%. Elemental analysis calcd for $\text{Ni}_4(\text{C}_{30}\text{H}_{24.5}\text{N}_7\text{O}_3)_4 \cdot 6\text{ClO}_4 \cdot 2\text{CH}_3\text{CN}$: H 3.45, C 49.03, N 13.83%. Found: H 3.46, C 48.95, N 13.81%. ESI–MS: m/z : 785.1693 $[\text{H}_3\text{Ni}_4(\text{FPB})_4]^{3+}$ (100%), 1177.2492 $[\text{H}_2\text{Ni}_4(\text{FPB})_4]^{2+}$ (53%).

Preparation of Ni–FMB. $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (36.5 mg, 0.10 mmol) and H_2FMB (46.3 mg, 0.10 mmol) were dissolved in $\text{CH}_3\text{CN}/\text{C}_2\text{H}_5\text{OH}$ (v/v = 9:1) to give a yellow solution. The solution was diffused with ether for several days at room temperature to give X-ray-quality light-yellow block crystals. Yield: 21%. Elemental analysis calcd for $\text{Ni}_4(\text{C}_{25}\text{H}_{19.5}\text{N}_6\text{O}_3)_4 \cdot 6\text{ClO}_4 \cdot \text{CH}_3\text{CN} \cdot 3\text{H}_2\text{O}$: H 3.21, C 44.80, N 12.81%. Found: H 3.24, C 44.65, N 12.77%. ESI–MS: m/z : 679.7817 $[\text{H}_3\text{Ni}_4(\text{FMB})_4]^{3+}$ (100%), 1019.1665 $[\text{H}_2\text{Ni}_4(\text{FMB})_4]^{2+}$ (76%).

Single-Crystal X-ray Crystallography. The intensities were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation source; the data were acquired using the SMART and SAINT programs.^{57,58} The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL version 5.1 software.⁵⁹

In the structural refinement of Zn–FPB, except for one partially occupied solvent CH_3CN molecule and all of the fluorine atoms in a disordered BF_4^- anion, all of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones and the solvent CH_3CN molecule were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. To assist the stability of refinements, the furan and benzene rings in the ligand, BF_4^- anions, and solvent CH_3CN molecule were restrained as idealized regular polygons, and the thermal parameters on adjacent atoms in furan and benzene rings were restrained to be similar. All the

fluorine atoms of a BF_4^- anion were disordered into two parts, with the s.o.f. of each part being fixed at free values. The SQUEEZE subroutine in PLATON was used.⁶⁰

In the structural refinement of Zn–FPB $\supset$ 1, except for one partially occupied solvent CH_3CN molecule and one partially occupied solvent water molecule, all of the carbon and fluorine atoms of a disordered CF_3SO_3^- anion and a 4-nitrobenzaldehyde substrate and all of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones, the substrate, and the solvent CH_3CN molecules were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. To assist the stability of refinements, one furan ring in the ligands and substrate, one CF_3SO_3^- anion, and one solvent CH_3CN molecule were restrained as idealized regular polygons, and thermal parameters on adjacent atoms in the furan ring and substrate were restrained to be similar. All of the carbon and fluorine atoms of a CF_3SO_3^- anion were disordered into two parts, with the s.o.f. of each part being fixed at free values.

In the structural refinement of Fe–FPB, except for one partly occupied solvent CH_3CN molecule and all of the oxygen atoms of a disordered ClO_4^- anion, all of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones and the solvent CH_3CN molecule were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. To assist the stability of refinements, the furan and benzene rings in the ligand, ClO_4^- anions, and solvent CH_3CN molecule were restrained as idealized regular polygons, and thermal parameters on adjacent atoms in the solvent CH_3CN molecule, partially disordered oxygen atoms of a ClO_4^- anion, and furan and benzene rings were restrained to be similar. All of the oxygen atoms of a ClO_4^- anion were disordered into two parts, with the s.o.f. of each part being fixed at free values. The SQUEEZE subroutine in PLATON was used.⁶⁰

In the structural refinement of Co–FPB, except for two partly occupied BF_4^- anions, all of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. To assist the stability of refinements, the furan and benzene rings in the ligand and BF_4^- anions were restrained as idealized regular polygons and thermal parameters on adjacent atoms in partially disordered fluorine atoms of two BF_4^- anions, and furan and benzene rings were restrained to be similar. All of the fluorine atoms in two BF_4^- anions were disordered into two parts, with the s.o.f. of each part being fixed at a free value. The SQUEEZE subroutine in PLATON was used.⁶⁰

In the structural refinement of Ni–FPB, except for two partially occupied solvent CH_3CN molecules and all of the oxygen atoms of a disordered ClO_4^- anion, all of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones and the solvent CH_3CN molecule were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. To assist the stability of refinements, the furan and benzene rings in the ligand, one ClO_4^- anion, and two solvent CH_3CN molecules were restrained as idealized regular polygons, and thermal parameters on adjacent atoms in furan and benzene rings were restrained to be similar. All of the oxygen atoms of a ClO_4^- anion were disordered into two parts, with the s.o.f. of each part being fixed at free values. The SQUEEZE subroutine in PLATON was used.⁶⁰

In the structural refinement of Ni–FMB, except for some solvent water molecules, all of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms within the ligand backbones, the solvent CH_3CN , ether, and ethanol molecule were fixed geometrically at calculated distances and allowed to ride on the parent non-hydrogen atoms. To assist the stability of refinements, two furan rings and one benzene ring in the ligands, ClO_4^- anions, and solvent CH_3CN , ether, and ethanol molecules were restrained as idealized regular polygons, and thermal parameters on adjacent atoms in furan rings were restrained to be similar. The furan and benzene rings in one ligand were disordered into two parts, with the s.o.f. of each part being fixed at free values. All the oxygen atoms of three ClO_4^- anions

were disordered into two parts, with the s.o.f. of each part being fixed at free values.

Photocatalytic Transfer Hydrogenation Protocol. The catalyst (0.1 mM, 0.5 μ mol), substrates (5.0 mM, 25.0 μ mol), NaBH_3CN (1.0 mM, 5.0 μ mol), and $\text{HCOOH}/\text{Et}_3\text{N}$ (0.1/0.05 M, 0.5/0.25 mmol) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1 in volume) were added to obtain a total volume of 5.0 mL in a 20 mL flask. The flask was degassed by bubbling argon for 15 min under atmospheric pressure at room temperature. The pH (8.5) of this solution was adjusted to a specific pH by adding H_2SO_4 or NaOH and measured with a pH meter. After that, the samples were irradiated with a 100 W LED lamp at 420 nm, and the reaction temperature was held at 298 K by using a water filter to absorb heat. The yields were determined by ^1H NMR analysis of the crude products.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b05351.

Complete experimental details and supporting figures; X-ray data for Zn–FPB (CCDC 1891712), Zn–FPB **1** (CCDC 1891711), Fe–FPB (CCDC 1891710), Co–FPB (CCDC 1891708), Ni–FPB (CCDC 1891709), and Ni–FMB (CCDC 1906243) (PDF) C124 H102 B4 F16 N30 O12 Zn4 (CIF) C145 H122 F24 N34 O40 S8 Zn4 (CIF) C120 H96 B4 Co4 F16 N28 O12 (CIF) C124 H104 Cl6 Fe4 N30 O36 (CIF) C128 H110 Cl6 N32 Ni4 O36 (CIF) C116 H130 Cl6 N26 Ni4 O47 (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21820102001, 21531001, and 21861132004). We thank the Shenzhen HUASUAN Technology Co., Ltd., for performing the DFT calculations and data analysis.

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