

Photoactive Chiral Metal–Organic Frameworks for Light-Driven Asymmetric α -Alkylation of Aldehydes

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1. Introduction

1.1 Toward green sustainable chemistry

Goal: Convert basic compounds into useful products in a sustainable fashion

For example... –Using more clean and cheap energy source

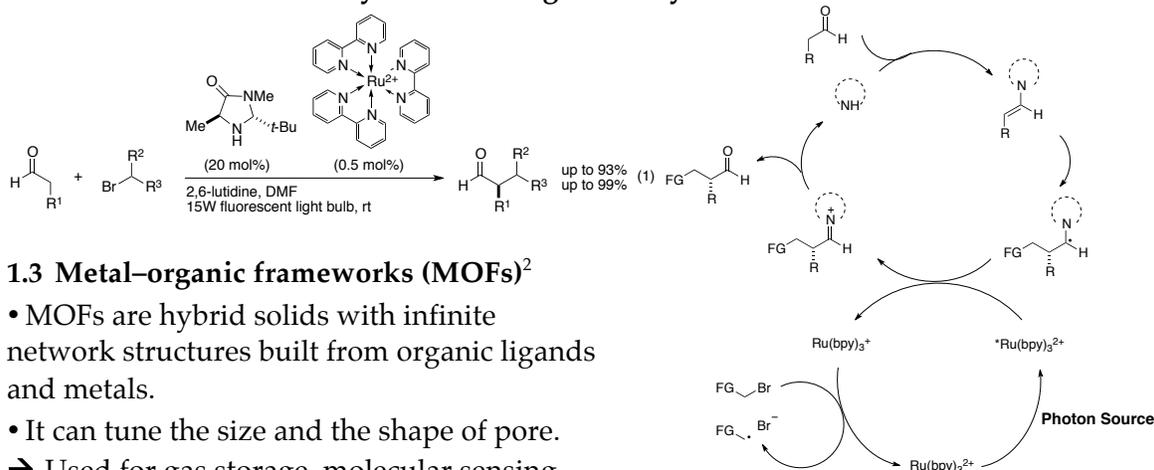
–Reuse catalyst to decrease the waste and cost

1.2 Photoredox catalysts with organocatalysts

• Recently, combination of organometallic complexes such as $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ir}(\text{ppy})_2(\text{dtbpy})]^+$ and organocatalysts are intensively investigated as an asymmetric photoredox catalysts (scheme 1).¹

→ Sunlight can be used as an inexhaustible light source ideally.

Scheme 1. Photoredox catalyst with an organocatalyst



1.3 Metal–organic frameworks (MOFs)²

• MOFs are hybrid solids with infinite network structures built from organic ligands and metals.

• It can tune the size and the shape of pore.

→ Used for gas storage, molecular sensing,

separation, medical applications and heterogeneous (asymmetric) catalysts.

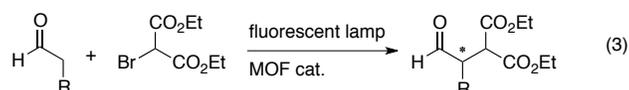
• MOFs can be reused for heterogeneous (asymmetric) catalyst.

1.4 This work

Incorporation of an asymmetric organocatalyst within a photoactive MOF

→ For constructing reusable photocatalytic systems

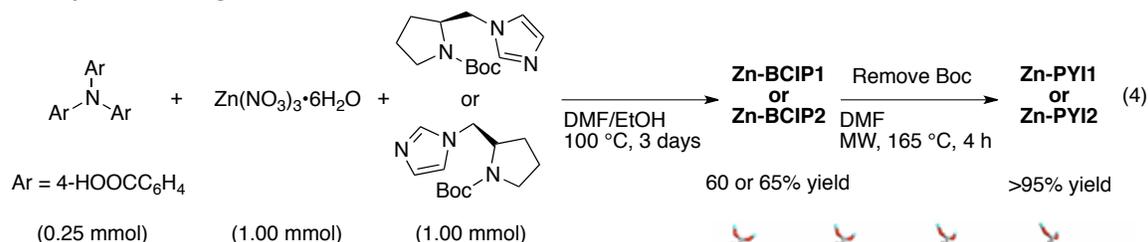
Strategy for this work



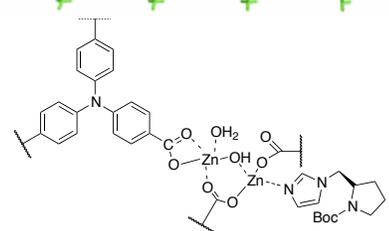
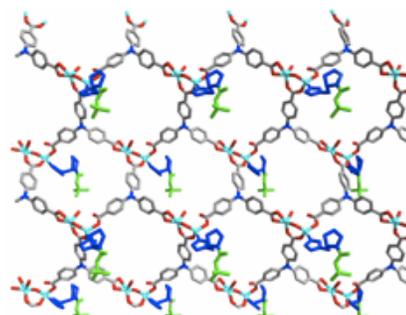
- Synthesizing MOF with photocatalyst, metal salt and asymmetric organocatalyst.
- They also synthesized MOF with only photocatalyst and metal salt to confirm installation of organocatalyst within a single MOF is crucial for enantioselectivity.

2. Results and Discussion

2.1 Synthesizing MOF (Zn-PYI1 and Zn-PYI2)



- **Zn-BCIP1** and **Zn-BCIP2** can be easily synthesized.
- Determined by elemental analysis and X-ray analysis (figure 1).
- Thermogravimetric analysis (TGA) of **Zn-BCIP1** exhibited a significant weight loss of 12.9% in the 100–200 °C.
- Boc group can be deprotected in 100–200 °C.
- The expulsion of the Boc group was further verified by ¹H NMR, IR and elemental analysis.



2.2 Nature of ZnPYI1

– Dye-uptake study

1. Soaking **Zn-PYI1** and **Zn-BCIP1** in a Fluorescein (2',7'-dichlorofluorescein)
2. Washing with solvent several times
3. Digesting fluorescein with sodium ethylenediaminetetraacetic acid
4. Quantified by UV the amounts of released fluorescein

- 14% of the framework weight of fluorescein was absorbed for **Zn-PYI1**, but fluorescein was not absorbed for **Zn-BCIP1**.

→ These results implied the releasing of channels during deprotection process.

– Circular dichroism (CD) spectrum

- **Zn-BCIP1** and **Zn-PYI1** showed cotton effect in each wavelength (figure 2, (a) and (b)).

- The peak around 340 nm was assignable to the absorbance corresponding to the π - π^* transition of the triphenylamine groups.

Figure 1. Crystal structure of Zn-BCIP1

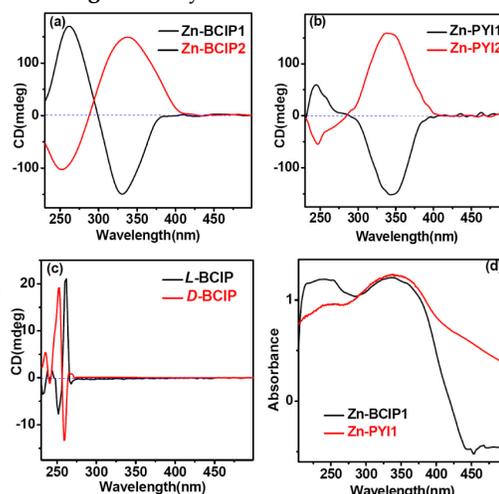


Figure 2. (a) CD spectrum of **Zn-BCIP1** and **2** (b) CD spectrum of **Zn-PYI1** and **2** (c) CD spectrum of **L-BCIP** and **D-BCIP** (d) UV spectrum of **Zn-BCIP1** and **Zn-PYI1**

– Redox potential of MOF

• The redox potential of the **Zn-PYI1⁺/Zn-PYI1^{*}** couple was -2.12 V (figure 3).

→ This potential was more negative than that of the diethyl 2-bromomalonate ($E^0 = -0.49$ V).

2.3 Absorption experiment (figure 4).

• The luminescence intensity of **Zn-PYI1** was significantly reduced when it absorbed diethyl 2-bromomalonate molecules (figure 4, (a)).

• Decrease of fluorescence lifetime of **Zn-PYI1** absorbed diethyl 2-bromomalonate molecules was observed (figure 4, (b)).

→ The quenching process was attributed to the photoinduced electron process from **Zn-PYI1^{*}** to diethyl 2-bromomalonate.

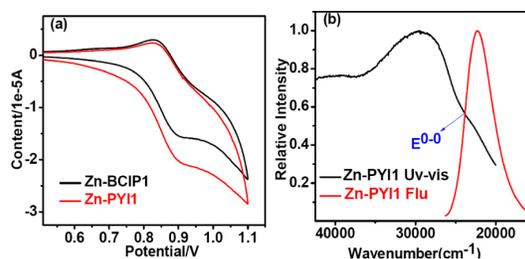


Figure 3. (a) Solid-state CV of **Zn-BCIP1** and **Zn-PYI1** with a scan rate of 50 mV s^{-1} in the scan range $0.5\text{--}1.1$ V. (b) Normalized absorption (black line) and emission spectra (red line) of **Zn-PYI1**, excited at 350 nm .

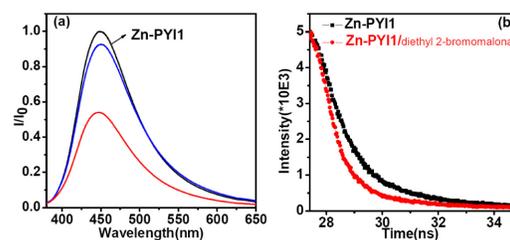
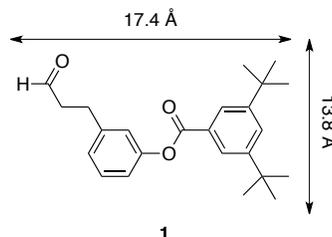
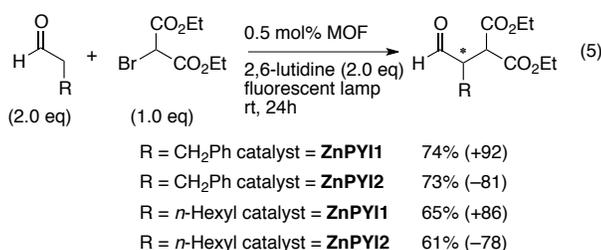


Figure 4. (a) Solid-state emission spectra of **Zn-PYI1** (black line), **Zn-PYI1** upon absorbance of phenylpropylaldehyde (blue line) and diethyl 2-bromomalonate (red line), excited at 350 nm . (b) Transient emission spectra of solid **Zn-PYI1** and **Zn-PYI1** with diethyl 2-bromomalonate incorporated.

2.4 Photocatalytic α -alkylation of Aliphatic Aldehydes



• **Zn-PYI1** and **Zn-PYI2** gave corresponding desired product in good yields with good ee values (in parentheses)

• When compound **1** whose size is larger than the pore size of **Zn-PYI1** was used, the desired reaction only gave the desired product in 7% yield.

→ The desired reaction took place mostly in the channel of the catalyst.

Control experiment for **Zn-PYI1**

- Reaction did not occur in the absence of fluorescent lamp.
 - **Zn-BCIP1** instead of **Zn-PYI1** did not afford the desired product.
 - The removal of **Zn-PYI1** by filtration shut off the reaction.
 - **Zn-PYI1** can be isolated by filtration and can be reused at least three times.
 - **Zn-PYI1** maintained the framework after the reaction.
- Confirmed by dye uptake study.

• Confirmation of heterogeneous and photocatalytic nature of the reactions.

2.5 Control Experiment

- To investigate the effect of combination of photocatalyst and organocatalyst within a single MOF, they synthesized Ho-based MOF.

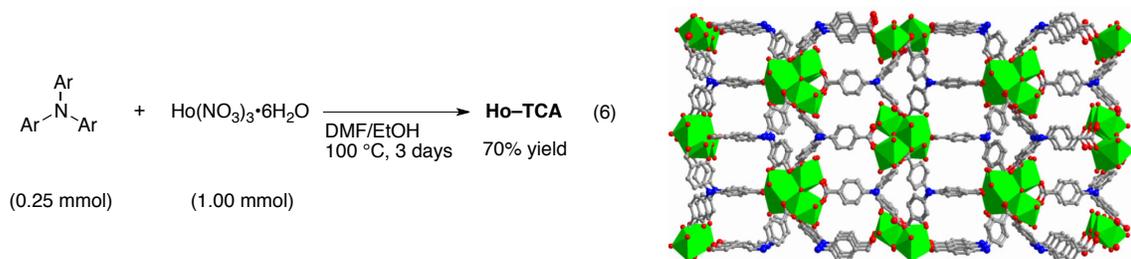
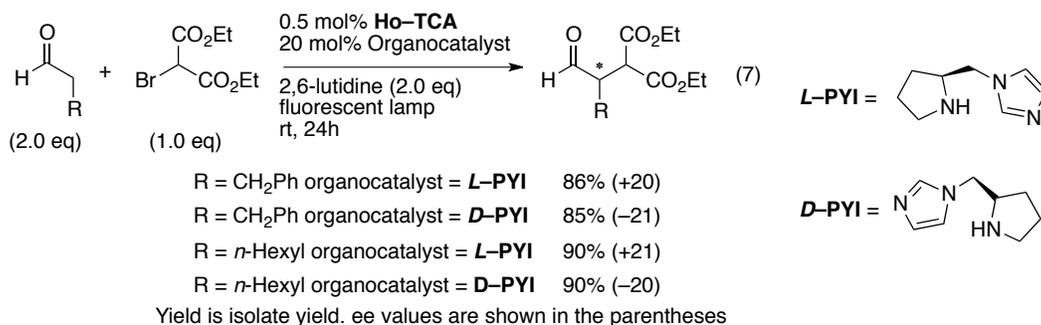


Figure 5. Structure of Ho-TCA

- Confirmed by elemental analysis and X-ray analysis.
- Dye-uptake studies showed a 23% uptake of fluorescein.
- Redox potential of the (Ho-TCA⁺/Ho-TCA^{*}) is -2.20 V. This is more negative than that of Zn-PYI1.

→ It is enough for photocatalytic reaction.



- The yield of the desired product is higher than that of Zn-PYI1 and Zn-PYI2.
 - ee values (in parentheses) dramatically got worse.
- This result suggests that incorporation of organocatalyst and photocatalyst within single MOF is effective for high enantioselectivity.

3. Conclusion

- MOF-based asymmetric photocatalyst through the cooperative combination of triphenylamine photocatalysis and proline-based asymmetric organocatalysis within a single MOF was developed.
- Control experiment showed that integration of photocatalyst and asymmetric organocatalyst into a single MOF is superior in the view of enantioselectivity.

4. References

- Nicewicz, D. A.; MacMillan, D. W. C. *Science*. **2008**, *322*, 77–80.
- Ferey, G. *Chem. Soc. Rev.* **2008**, *37*, 191–214.