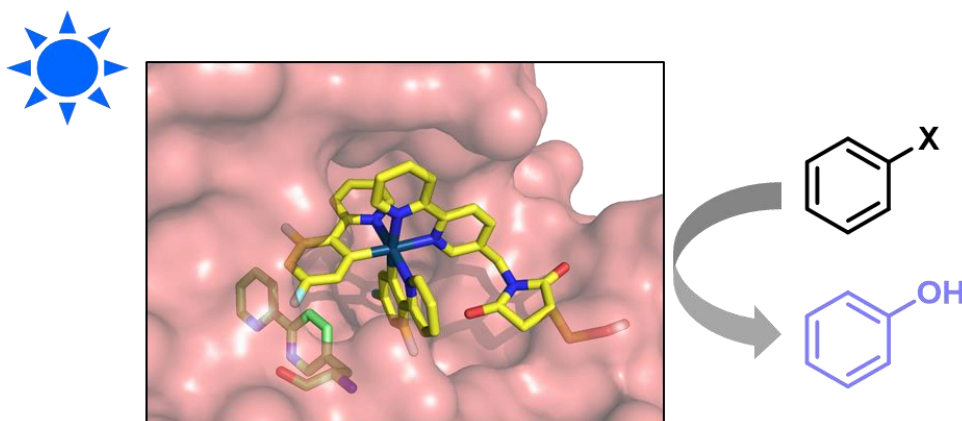


Molecular Design of Photocatalytic Cross-coupling Enzymes

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Photocatalytic reactions using light energy for chemical production have been a long-standing goal in catalyst design.¹ Herein, we synthesized artificial metalloenzymes by introducing an Ir photocatalyst and a Ni(bpy) complex to an optimal protein scaffold.² Consequently, the photocatalytic enzyme generated C–O coupling products with up to 96% yields by harvesting visible light and performing intramolecular electron transfer between the two catalysts. We rationally modulated the catalytic activities of the artificial photocatalytic cross-coupling metalloenzymes by tuning the electrochemical properties of the catalytic components, their positions, and distances within a protein. As a result, we discovered the mutant that showed broad substrate scopes under optimized conditions. This work explicitly demonstrated that we could integrate and control the inorganic and biochemical components of photocatalytic biocatalysis to achieve high yield and selectivity in valuable chemical transformations.



References

¹ Chan, A. Y.; Perry, I. B.; Bissonnette, N. B.; Buksh, B. F.; Edwards, G. A.; Frye, L. I.; Garry, O. L.; Lavagnino, M. N.; Li, B. X.; Liang, Y.; Mao, E.; Millet, A.; Oakley, J. V.; Reed, N. L.; Sakai, H. A.; Seath, C. P.; MacMillan, D. W. C. *Chem. Rev.* **2022**, *122*, 1485–1542.

² Lee, J.; Song, W. J. *J. Am. Chem. Soc.* **2023**, *145*, 5211-5221.