Selective Photocatalytic Reactions Based on Confinement Effects with a Visible-Light-Active Pt(II)-Cornered Hollow Cage

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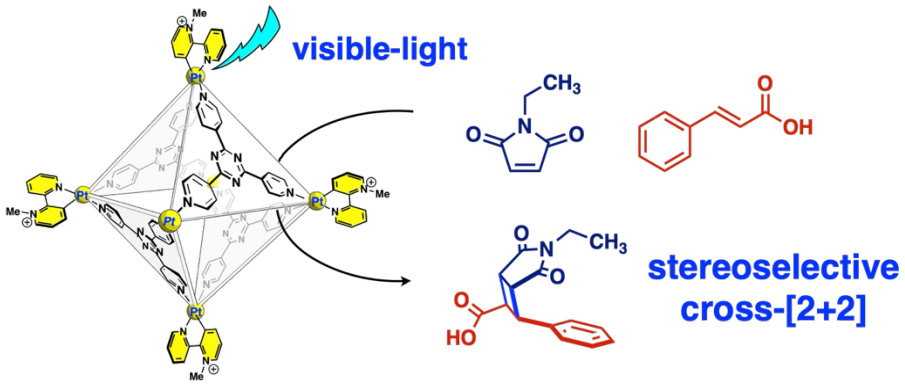
Photoreactions within a cage compound enable unique molecular transformations based on confinement effects[1]. Most of them, however, require UV light, which limits substrate scope and selectivity. Recently, we reported a visible-light-active M_6L_4 cage constructed from a cyclometalated Pt(II) complex, combining host-guest recognition, conformational control, and visible-light activity (CSJ 104th, F1232-4am-14).

Herein, we report a stereoselective and efficient visible-light-induced [2+2] cycloaddition reaction using the visible-light-active cage. Stirring the cage with substrates in water yielded a ternary inclusion complex with well-defined geometry. Under blue-light irradiation at room temperature, a [2+2] cycloaddition proceeded quantitatively to afford a *syn* isomer. The introduction of a cyclometalated Pt(II) vertex contributed to improved reactivity compared to conventional M_6L_4 cages without visible-light activity. Further optimization enabled the unprecedented stereoselective catalytic [2+2] cycloaddition of cinnamic acid with maleimides. Mechanistic studies revealed that the reaction proceeded via energy transfer from the cage to the encapsulated substrates.



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