

Supporting Information

The Role of Metal-Organic Porous Frameworks in Dual Catalysis

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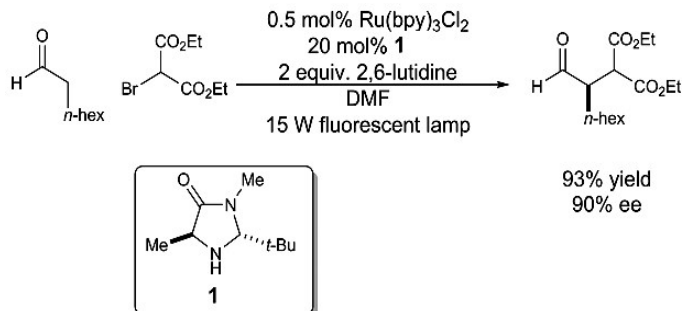
Table S1. Types of dual-site catalyses by homogeneous catalysts in photochemical processes.¹

The Classification of Photochemical Dual Catalysis							
Photoinduced Electron Transfer Redox Mediation Photooxygenation Alkene oxidation Heteroatom oxidation Oxidative rearrangement Photoreduction Example 1. Redox-Mediated Cyclopropane Photooxygenation. <table border="1" style="margin: 10px auto;"> <thead> <tr> <th>BP</th><th>Reaction Time</th></tr> </thead> <tbody> <tr> <td>0 mol%</td><td>19 h</td></tr> <tr> <td>100 mol%</td><td>1.5 h</td></tr> </tbody> </table> biphenyl (BP) Lewis Acid Catalysis Substrate–Lewis acid interactions Photocatalyst–Lewis Acid interactions Lewis acid catalysis of non-redox steps Example 2. Ru(bpy)₃Cl₂/Mg(ClO₄)₂-Catalyzed [4+2] Bis(enone) Cycloaddition. Brønsted Acid/Base Catalysis Proton-coupled electron transfer (PCET) Brønsted acid catalysis of non-redox steps Example 3. Nitroarene Reduction and Post-PET Cyclization. 1 camphorsulfonic acid (CSA)	BP	Reaction Time	0 mol%	19 h	100 mol%	1.5 h	
BP	Reaction Time						
0 mol%	19 h						
100 mol%	1.5 h						

Organocatalysis

Enamine/iminium catalysis
Hydrogen atom-transfer (HAT) catalysis
Other modes of organocatalysis

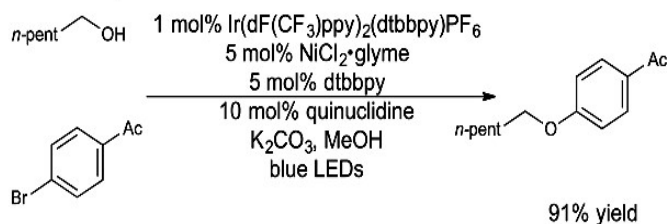
Example 4. Aldehyde-Alkylation by Tandem Photo-/Organocatalysis



Transition Metal Catalysis

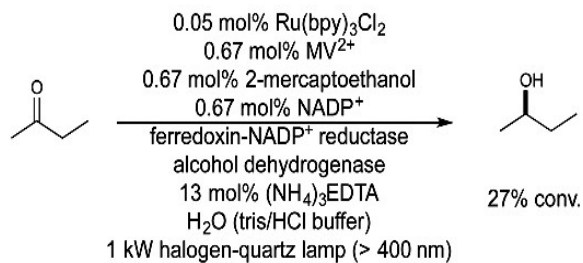
Catalysis of Redox Steps
Catalysis of Downstream Steps

Example 5. Nickel-Catalyzed Cross Coupling Enabled by Photocatalysis.



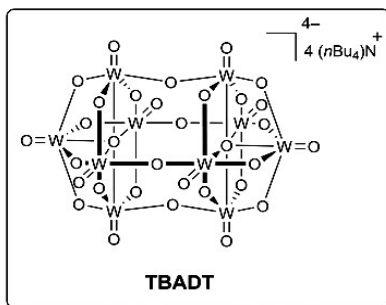
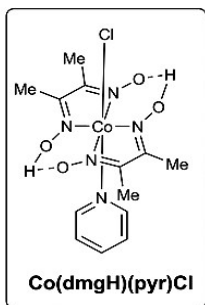
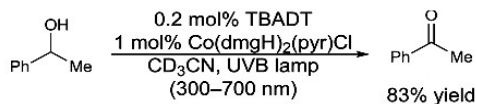
Enzymatic Catalysis

Example 6. Enzymatic/Photocatalytic Ketone Reduction.



Photoinduced Hydrogen Atom Transfer

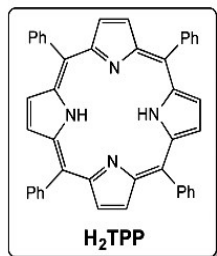
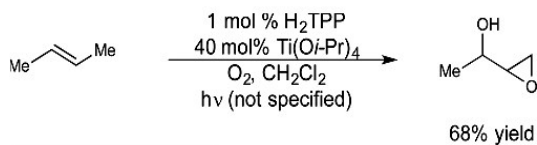
Example 7. Alcohol Dehydrogenation by Tandem Polyoxotungstate and Cobaloxime Catalysis.



Photoinduced Energy Transfer

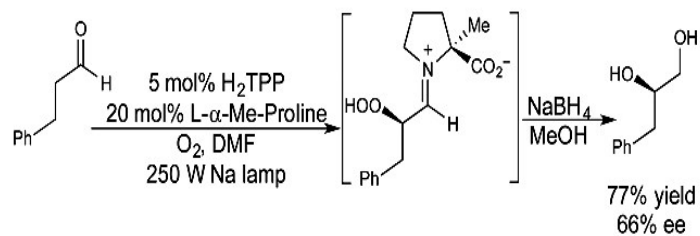
Transition Metal Catalysis

Example 8. Tandem Allylic Oxidation and Alkene Epoxidation.



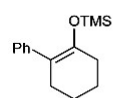
Organocatalysis

Example 9. Aldehyde α -Oxygenation by Dual Enamine and Photocatalysis.



Brønsted Acid Catalysis

Example 10. Silyl Enol Ether Protonation by Photosensitized Naphthol.



2.5 mol% Ir(dFppy)₂(pic)
50 mol% 2-naphthol
excess NHS
toluene, laser (445 nm)



74% yield

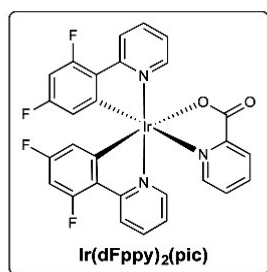


Table S2. Types of dual-site MOF catalysis in multi-step catalytic reactions.

Entry	MOF Catalysts:Active sites	Catalytic Reactions	Ref.
1	Au/MIL-53(Al): acid site and metal NPs	Oxidation along with hydrogenation	2
3	Zr-MOF-NH ₂ : base and acid sites	Knoevenagel and aldol condensations	3
4	Sc-MOF: acid sites	Epoxidation along with rearrangement	4
5	MIL-101-SO ₃ H-NH ₂ and PCN-124: base and acid sites	Deacetalization along with Henry or Knoevenagel condensations	5,6
6	NH ₂ -MIL-101(Al): base and acid sites	Meinwald rearrangement along with Knoevenagel	7
7	Pd/MIL-101	Aldol condensation along with hydrogenation	8
8	Tb-TCA and Pd@IRMOF-3: acid, base and metal NPs	Knoevenagel condensation along with cyclization or hydrogenation	9 10
9	IRMOF-3: base and acid sites	Condensation along with addition	11
10	Pd/MIL-101(Cr): metal and acid site	Nitro reduction along and cyclization	12
11	Pd/MIL-101: acid site and metal NPs	Hydrogenation along with isomerization Coupling and cyclization	13, 14
13	Pd@MIL-101(Cr): acid site and metal NPs	Isomerization and hydrogenation	15
14	Ru-PTA/MIL-100(Cr): acid site and metal NPs	Hydrolysis and hydrogenation	16
15	UiO-67-NH ₂ -[L3Rh]: base site and metal complex	Condensation/olefin-hydrogenation/nitro-reduction	17
16	UiO-66-Lir: base site and metal complex	Reductive-amination/condensation/hydrogenation of imine	18

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