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# 화학과 대학원 세미나

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## Catalytic Functionalization of Nitrogen Compounds:

### From Selective C–H Amination to Photocatalytic Ammonia Synthesis

Nitrogen-containing molecules are of great importance in the field of organic chemistry, inorganic synthesis, and material science owing to their unique chemical and physical properties.<sup>1</sup> In this talk, I will showcase how a well-defined molecular catalyst could give an efficient and selective access to various classes of nitrogen compounds. In the first part of the talk, mechanistically driven discovery of novel class of amide agents will be discussed. Extensive Investigation on rhodium-catalyzed C–H amidation with organic azide led us to introduce 1,4,2-dioxazol-5-ones as highly efficient amide precursor.<sup>2</sup> An integrated low-temperature NMR kinetics and computational study revealed a key role of high-valent metal-nitrenoid intermediate,<sup>3</sup> and further efforts to utilize its reactivity enabled to design a new array of iridium catalysts for  $\gamma$ -lactam formation.<sup>4</sup> Asymmetric<sup>5</sup> and site-selective<sup>6</sup> catalysis has been also achieved by utilizing noncovalent interactions. The second part of the talk will focus on the development of bifunctional photocatalysts for ammonia synthesis. Proton-coupled electron transfer using molecular hydrogen as a terminal reductant is an attractive strategy for synthesizing weak element-hydrogen bonds, but the intrinsic thermodynamics presents a challenge for reactivity. I will describe the direct photocatalytic synthesis of weak element-hydrogen bonds of unsaturated organic molecules<sup>7</sup> as well as metal-nitrogen compounds.<sup>8</sup> Activation of molecular hydrogen occurs in the ground state and the resulting iridium hydride harvests visible light to enable spontaneous formation of weak chemical bonds near thermodynamic potential without any by-product. Transient absorption spectroscopic studies revealed a triplet-triplet energy transfer as the photophysical initiation process. Identification of catalyst deactivation pathway led to a design of the next-generation catalyst with improved photostability and better catalytic performance.<sup>9</sup>

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