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## Advances in Organic and Inorganic Photoredox Catalysis

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Visible light is perceived as an ideal source of energy to activate organic and inorganic compounds and mediate photophysical and photochemical transformations. In the early 20th century, Ciamician reported his vision to exploit the renewable energy potential of visible-light irradiation as a strategy for sustainable chemical development.<sup>1</sup> However, the lack of color for most organic and inorganic molecules and their transparency to visible light has impeded progress toward this goal. Although the UV irradiation of organic and/or inorganic compounds has allowed the development of efficient organic<sup>2</sup> and inorganic photochemical reactions,<sup>3</sup> this approach suffers from poor functional group tolerance and harnesses less than 10% of the solar power potential.<sup>4</sup> Over the past 20 years, a great deal of research has been devoted to triggering chemical transformations with abundant and chemically inert visible light.

Inorganic materials such as TiO<sub>2</sub> were initially reported to be potent photocatalysts,<sup>5</sup> and in the 1970s, Fujishima and Honda reported an important contribution on solar water-splitting and carbon dioxide reduction, which stimulated the field of research on semiconductor photocatalysts.<sup>6</sup> During the same period, the selected activation of small organic molecules by visible-light-absorbing organometallic photocatalysts was also demonstrated by several researchers, thereby establishing the foundations for visible-light homogeneous photocatalysis.<sup>7</sup> However, while research on semiconductor photocatalysts progressively increased,<sup>8</sup> the concept of photocatalysis in the field of organic chemistry remained undiscussed until 2008/2009, when MacMillan, Yoon, and Stephenson demonstrated significant advances, illustrating its significant potential for the research community.<sup>9</sup> Since then, photoredox catalysis has been extensively developed in organic and inorganic chemistry, and even in other fields of science.

We are pleased to launch this issue of *ACS Organic & Inorganic Chemistry Au*, which includes selected Reviews and Articles covering key topics and *advances in organic and inorganic photoredox catalysis*.

Several Articles and Reviews in this issue are dedicated to the preparation of new photocatalysts. Chiral-at-metal Lewis acid catalysts, in which the chiral information comes from the metal center, have been shown to be useful in a wide range of enantioselective metal-catalyzed reactions, as discussed in the in-depth and insightful Review from Biplab Maji et al.<sup>10</sup> Chiral-at-metal photocatalysts have been successfully employed in several important enantioselective transformations, and their huge contribution to the recent progress of asymmetric photoredox catalysis is presented. The Review also provides a critical analysis of the topic and outlines future directions for the field.

This issue contains reports on novel metal or organo-photocatalysts and their applications (mainly in organic chemistry). Designing photoredox catalysts that absorb in the red-light region has recently stimulated intensive research toward broad biological applications. Katarzyna Rybicka-Jasińska and Dorota Gryko et al. disclose the opportunities offered by free-base porphyrin photocatalysts to functionalize biomolecules under red light irradiation.<sup>11</sup> They demonstrate that free-base porphyrin can serve both as a photo-oxidant and reductant in various organic reactions. Moreover, the development of phosphorescent organometallic compounds emitting in the deep red to near-infrared has been the subject of intensive research in recent years. In this context, new heteroleptic bis-cyclometalated iridium complexes have been synthesized and studied by Thomas S. Teets et al.<sup>12</sup> In addition, several efforts have been made to develop metal-free photocatalysts with similar redox properties to metal-based ones. In this vein, Till Opatz et al. report a two-step synthesis of polyazahelicene, which displays high reductive ability. Its efficiency as a photoreductant has been demonstrated in two multicomponent reactions and shows similar activity to Ir(ppy)<sub>3</sub> photocatalysts.<sup>13</sup> The immobilization of metal-based photocatalysts is also a complementary approach to develop more eco-friendly transformations and has been the subject of intensive research in organic and inorganic chemistry. In this issue, Kelly Materna and Carl-Johan Wallentin et al. present the application of heterogeneous iridium-on-alumina as a photoredox catalyst in a set of five model reactions (reductive dehalogenation, atom-transfer radical addition, aerobic oxidative hydroxylation of boronic acids, oxidative fragmentation of ethers and acetals, and the *E*–*Z* isomerization of cinnamates).<sup>14</sup> The results show that this supported photoredox catalyst displays excellent activity, higher than that of the homogeneous catalyst, with good recyclability properties. Molybdenum disulfide (MoS<sub>2</sub>) quantum dots (QDs) have attracted significant attention for application in photocatalytic water splitting for H<sub>2</sub> generation. However, recently they have found application in photoredox transformations of organic compounds. De et al. disclose in their Article that MoS<sub>2</sub> QDs are an efficient photocatalyst for the C–H functionalization of tetrahydroisoquinolines with indoles (or phosphites). Detailed

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mechanistic studies suggest that after irradiating MoS<sub>2</sub> QDs, the excited electron in the conduction band can trigger the oxidation of amines in the presence of O<sub>2</sub>.<sup>15</sup> DFT calculations are useful for designing high-performance catalysts and better understanding catalytic activity. In that regard, Theresa McCormick et al. demonstrate the value of computational studies as a tool for fine-tuning photoredox catalysts, namely tuning Ni(II) tris-pyridinethiolate for water splitting.<sup>16</sup> This study provides insight into the structure of the catalyst with the formation of various isomers after the protonation of different possible sites on the Ni(II) complex.

The development of new synthetic reactions using known organic or inorganic photocatalysts is also included in this issue. Gary Molander et al. present recent advances in photoinduced chemical reactions involving 1,2-radical shifts.<sup>17</sup> This Review provides an excellent overview of the recent synthetic applications of this radical process, with special emphasis on understanding the mechanism and its utility for the synthesis of organic molecules. Then, Maurizio Fagnoni et al. describe recent progress in visible-light-promoted selenylation, presenting useful radical methodologies for C(sp<sub>2</sub>)-Se bond and C(sp<sub>3</sub>)-Se bond formation.<sup>17</sup> The authors also highlight the need to develop new photocatalytic synthetic procedures to form (sp<sub>3</sub>)-Se bonds. Two Articles dealing with a related subject, the formation of C(sp<sub>2</sub>)-S and C(sp<sub>3</sub>)-S bonds, discuss the use of diazonium salts as precursors of aryl radicals. Yevheniia Markushyna and Aleksandr Savateev et al. report the efficient synthesis of sulfonyl chlorides using potassium poly(heptazine imide) as a photocatalyst.<sup>18</sup> Using this cheap and available heterogeneous organocatalyst, they describe a novel Sandmeyer-type transformation between thiols and arenediazonium salts with good functional group tolerance on the aromatic rings. Samir Messaoudi et al. have developed a photoredox-catalyzed Stadler-Ziegler arylation of thiosugars with *in situ*-generated diazonium salts from anilines. This protocol affords direct access to various S-aryl thioglycosides, which are valuable building synthons for drug discovery and chemical biology.<sup>19</sup>


The visible-light photocatalytic functionalization of alkenes is a useful procedure for preparing high-value organic compounds. Zhu et al. present an efficient method for synthesizing allylic and homoallylic azides through the visible-light-promoted photoredox-mediated difluoroalkylation of trisubstituted alkenes with ethyl bromodifluoroacetate. The reaction allows the functionalization of internal alkenes, leading to the formation of allylic or homoallylic products according to the substitution of alkenes.<sup>20</sup>

Visible-light mediated [2 + 2] cycloaddition via energy transfer mechanism is a valuable method for the synthesis of highly strained cyclobutanes. Here, Olga García Mancheño et al. disclose intermolecular [2 + 2] photocycloaddition reactions between enamides and styrenes for the direct synthesis of unnatural 2-substituted cyclobutane  $\alpha$ -amino acids.<sup>21</sup> The method employs [[Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>dtbpy]PF<sub>6</sub>] as a photoredox catalyst, and a variety of cyclobutanes were prepared in good yields. In addition, Christoforos Kokotos et al. report the synthesis of cyclobutanes via [2 + 2] cycloaddition between N-aryl maleimides and styrenes, catalyzed by thioxanthone as an organic sensitizer. Interestingly, no catalyst was needed to promote the reaction when N-alkyl maleimides were used as a partner. A range of cyclobutanes were prepared (with or without photocatalyst) in good yields with moderate diastereoselectivity.<sup>22</sup>

The combination of photoredox catalysis with other catalysis modes offers exciting opportunities for the development of new transformations. For instance, Alfonso Carotenuto, Diego Brancaccio, and Mariateresa Giustiniano et al. develop a photoredox-catalyzed amide formation between *N*-methyl-*N*-alkyl aromatic amines and isocyanides in an aqueous micellar medium.<sup>23</sup> Based on intensive NMR studies, the formation of photoactive micelles was proposed due to an interaction between photocatalyst and surfactant, which opens new exciting perspectives in the photoredox catalysis field. Cyril Ollivier, Virginie Mouriès-Mansuy, and Louis Fensterbank et al. present a dual catalytic system combining a visible-light photoredox catalyst and a silver(I) salt for the synthesis of 3-sulfonylindoles.<sup>24</sup> The process relies on the 5-endo-dig cyclization of ortho-alkynyl *N*-sulfonyl precursors with a concomitant 1,3-sulfonyl migration. During optimization, when gold(I) salt was used instead of silver(I) salt, they observed that no photocatalyst was needed for this transformation.

Nowadays, photocatalyst-free strategies have attracted extensive attention, and here, three Articles illustrate the potential of these strategies in photochemical synthesis. Takahiko Akiyama et al. accomplished C(sp<sub>2</sub>)-S bond formation by exploiting the C-H functionalization of alkanes via electron donor-acceptor EDA complex photoexcitation.<sup>25</sup> Several experiments establish the formation of an EDA complex between the electron-rich thiolates and a sacrificial acceptor (electron-poor arene). This EDA-complex-initiated free-radical reaction allows access to structurally diverse thioethers in good yields. Indranil Chatterjee et al. also report EDA complex formation through *N*-bromosuccinimide additives to promote the visible-light-driven C-H functionalization of tetrahydrofuran derivatives.<sup>26</sup> A broad range of radical acceptors, including  $\alpha$ -diazoketones, azodicarboxylates, and aryl and allyl sulfones, were well tolerated affording efficient access to  $\alpha$ -functionalized tetrahydrofurans. An alternative photocatalyst-free strategy involved introducing photoactivable functional groups into organic molecules to trigger radical transformations. An additional example of a photocatalyst-free strategy is presented by Stefano Protti et al., who describe the use of arylazo sulfones as visible-light photoactivable substrates to photochemically arylate various enol silyl ethers and ketene silyl acetals.<sup>27</sup> This report provides a novel and general approach for the synthesis of  $\alpha$ -arylated ketones and esters under mild conditions.

The contributions in this issue outline some recent exciting developments in photoredox catalysis, encompassing organic, organometallic, and inorganic chemistry, reporting new compounds, insight, and transformations. We wish to thank each of the researchers who contributed their exciting work to this collection and thank the reviewers for their valuable insight. We hope you enjoy reading this issue!

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## Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

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