

Preview

Long-wavelength photocatalysis enabled by an *in-situ*-assembled manganese platform

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Advances in long-wavelength photocatalysis have drawn significant attention within organic synthesis. In this issue of *Chem*, Niu and co-workers describe a manganese-based long-wavelength photocatalytic platform that mediates alkene oxygenation and nitrogenation through a modular *in situ* assembly approach. The utility of this platform is demonstrated by its wide substrate scope, scalability, and efficient late-stage functionalization.

Recent developments in visible-light photocatalysis have highlighted the importance of accessing longer-wavelength irradiation for improved functional-group compatibility.^{1–3} In particular, photocatalysis driven by long-wavelength light ($\lambda > 595$ nm) has emerged as a promising regime for achieving such enhanced tolerance.⁴ Such mild excitation conditions minimize undesired side reactions, including overfunctionalization or degradation, while enabling deeper penetration through various media.⁵ Although it is often described as low-energy photocatalysis, we advocate for the term “long-wavelength photocatalysis” or “low-photon-energy photocatalysis” to explicitly distinguish the spectral energy of individual photons from the total energy dependent on source intensity.

Nevertheless, the development of long-wavelength photocatalysis still remains relatively underdeveloped. Previously reported long-wavelength photocatalysts often require multiple preparative steps, including ligand and complex synthesis.⁶ Moreover, these preparations should be repeated iteratively until photocatalytic performance is achieved. Such extensive preparation hampers overall process efficiency and underscores the need for readily tunable and accessible long-wavelength photoredox platforms.

As described in this issue of *Chem*, Niu and co-workers utilized a modular *in situ*

assembly strategy to develop a long-wavelength photocatalytic platform (Figure 1A)⁷ that enables direct evaluation of photoredox activity and the subsequent development of related catalytic transformations. Using this approach, the authors reported a manganese-based assembly for the oxygenation and nitrogenation of alkenes via 850-nm-light-induced azido radical generation.

The authors could readily access a wide range of assemblies by varying the metal salt, ligand, substrate, and additive, thereby enabling facile tuning of light-absorbing properties. To identify candidates suitable for long-wavelength photoredox catalysis, they directly evaluated each assembly by UV-visible (UV-vis) spectroscopy to examine absorption in the long-wavelength region (Figure 1B, i). Importantly, any readily available ligands, including substrates or additives, could serve as building blocks within the assembly, offering additional handles for tuning the absorption profile. Among the assemblies screened, the combination of manganese carbonate (MnCO_3), 2,2'-bipyridine (bpy), azidotrimethylsilane (TMSN_3), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) exhibited pronounced absorption near 850 nm. Notably, HFIP played a key role in extending the absorption into this long-wavelength region.

After identifying a Mn-based assembly capable of absorbing long-wave-

length light, the authors next investigated the photoredox activity by UV-vis measurements (Figure 1B, ii). Monitoring under 850-nm light in N_2 revealed a gradual decrease, indicating photoinduced azido radical generation. Upon subsequent introduction of O_2 , the absorbance recovered, implying the regeneration of the original catalytic assembly. This platform successfully transformed a wide range of alkene substrates into ketonitriles, ketones, and nitriles under 850-nm irradiation in the presence of O_2 . The authors also proposed a plausible reaction pathway supported by additional mechanistic studies and density functional theory (DFT) calculations.

To further showcase the synthetic utility of the *in-situ*-assembled Mn-based long-wavelength photoredox platform, the authors carried out a series of representative experiments (Figure 1C). Photocatalytic isotope labeling proceeded with high efficiency (96%), and gram-scale synthesis in a conventional flask was also successfully achieved (73%). These results underscore the potential applicability of this system, particularly given the intrinsic biocompatibility associated with long-wavelength light. Moreover, compared with short-wavelength visible light (445 nm), the 850-nm irradiation exhibited superior penetration through animal tissues and artificial materials, highlighting a distinct advantage



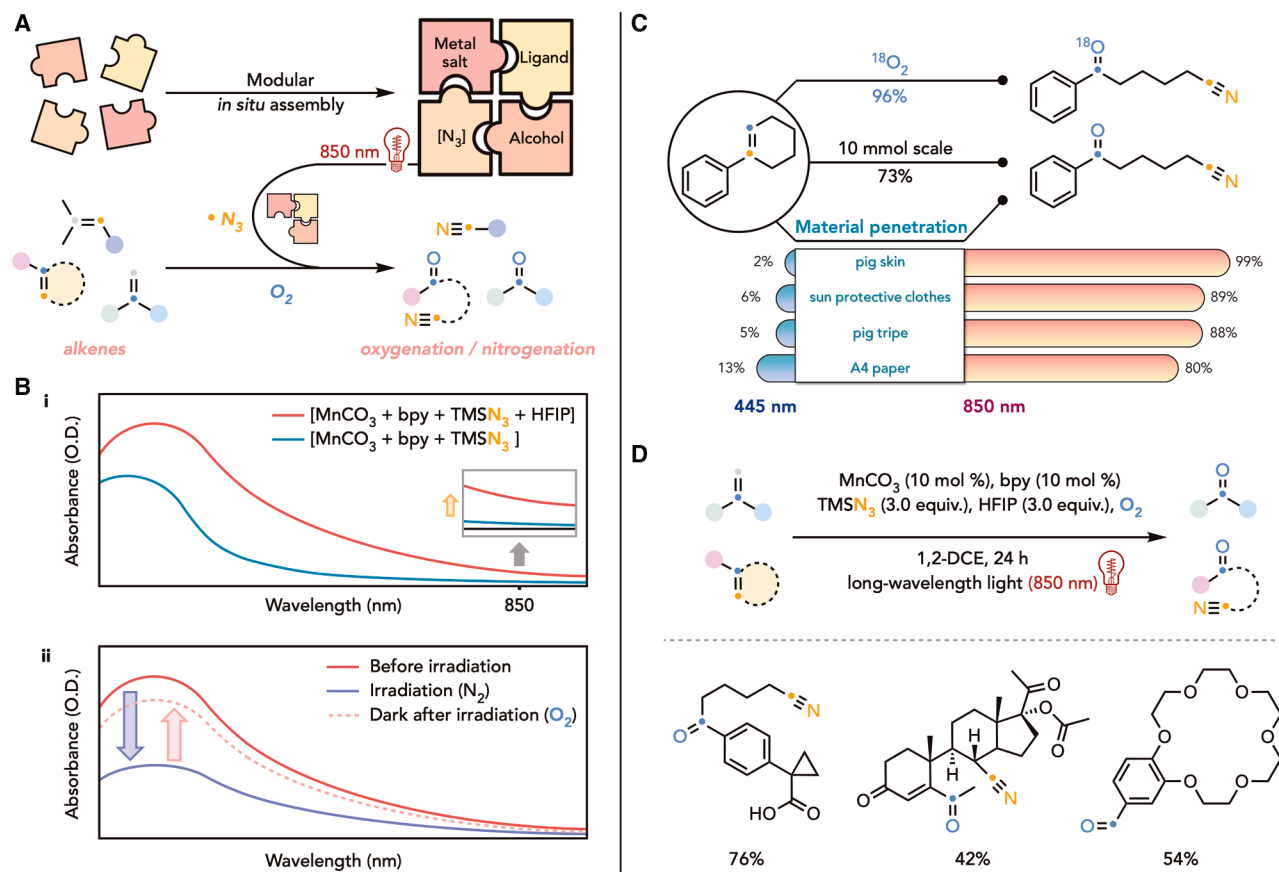


Figure 1. Mn-based long-wavelength photocatalytic platform and its synthetic practicality

(A) *In situ* assembly platform.
 (B) UV-vis measurements.
 (C) Synthetic utility.
 (D) Representative substrate scope.

of this platform for biomedical and polymer-related applications.^{8,9}

Building on these features, the authors further evaluated the practicality of the protocol in synthetic organic chemistry (Figure 1D). The photoredox platform with long-wavelength light exhibited markedly improved tolerance toward sensitive functional groups, including carboxylic acids (76%). In addition, the platform allowed the late-stage functionalization of a steroid-based substrate (42%) and the transformation of an 18-crown-6-based phase-transfer catalyst (54%).¹⁰ These results illustrate the versatility of this platform and its potential utility in medicinal and materials chemistry.

In summary, Niu and co-workers established a user-friendly and tunable modular *in situ* assembly strategy that

enables the development of an innovative long-wavelength photoredox catalytic platform. Through this approach, the authors achieved the oxygenation and nitrogeneration of diverse alkenes via azido radical generation. Moreover, long-wavelength excitation imparted superior penetration and enhanced functional-group tolerance. The synthetic utility of this platform was further demonstrated by the broad substrate compatibility, scalability, and effective late-stage functionalization. We envision that this work will facilitate the straightforward development of new long-wavelength photocatalytic platforms with versatile applicability.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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