Donor-acceptor complex enables alkoxyl radical generation for metal-free inert bond functionalizations

With the support by the National Natural Science Foundation of China, the research group led by Prof. Chen Yiyun (**陈以昀**) from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences demonstrates that the donor-acceptor complex enables metal-free inert bond functionalizations, which was published in *Angew Chem Int Ed* (2017, 56(41): 12619－12623).

The alkoxyl radical is an essential and prevalent reactive intermediate for chemical and biological studies, however its traditional generation requires heating, strong oxidants, or UV light irradiation. The group led by Chen previously discovered that the alkoxyl radical can be generated under mild photoredox catalysis conditions, however the heavy-metal photocatalysts are required which compromise itssynthetic, material, and biological applications.

Herein Chen's group reports the first donor-acceptor complex approach to enable alkoxyl radical generation under metal-free reaction conditions. Hantzsch ester forms the key donor-acceptor complex with N-alkoxyl derivatives, which shows bathochromic shift in absorption and induces the photocatalyst-free reactivity under visible light irradiation. Selective C(sp^3)－C(sp^3) bond cleavage and allylation/alkenylation is demonstrated for the first time using this approach *via* linear primary, secondary, and tertiary alkoxyl radicals. They envision this donor-acceptor complex approach will be instrumental for new visible-light-induced reaction design and novel metal-free inert bond functionalizations.

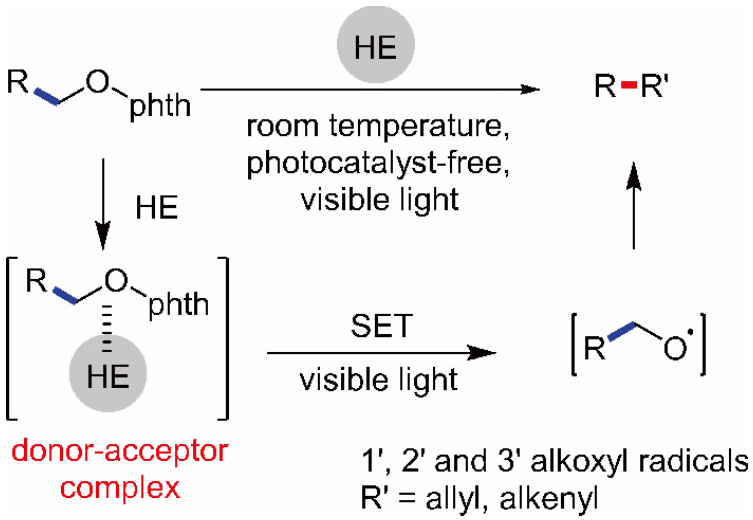

Figure Metal-free inert chemical bond functionalization via donor-acceptor complex.