

Porphyryns as photoredox catalysts in efficient C-C bond formation

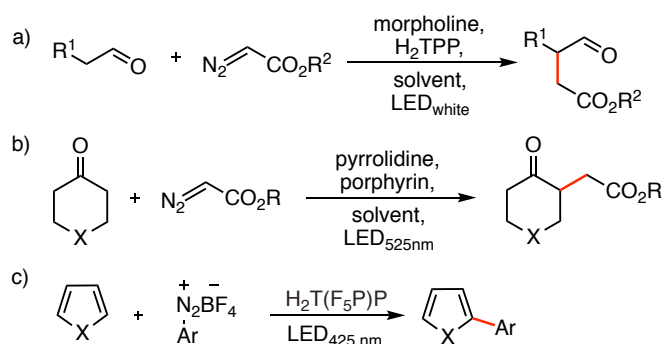
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The following dissertation focuses on the development of new organic, photoredox catalysts. I envisaged that porphyrins with their 18 π -electron aromatic macrocycle are perfectly suited for this role because they a) absorb visible-light, b) have high absorption coefficient, c) exhibit a small singlet-triplet splitting, d) have high quantum yield for intersystem crossing, e) and possess longer lifetime of the triplet state in comparison to the singlet state, not to mention straightforward synthesis. After light absorption porphyrins are excited to the triplet state and at this state they are able to transfer energy (photosensitization) or electrons (photoredox catalysis). These properties have been broadly used in the generation of singlet oxygen, conversion of solar energy, and in water splitting but before 2016 there were no example describing their use in C-C bond forming reactions through the porphyrin ring oxidation and reduction to ion radicals.

The main goal of my research was to establish a solid background for porphyrin's as photoredox catalysts that can be utilized in C-C bond forming reactions.

Herein, I demonstrate a successful application of these compounds as efficient photoredox catalysts for C-C bond forming reactions involving the reductive or oxidative quenching. Employing dual catalytic system – photocatalysis merged with enamine-iminium catalysis alkylation of aldehydes and ketones at the α position was accomplished (reductive quenching) (Scheme 1a, b). I have also found that porphyrins are also effective in catalyzing light-induced direct arylation of heteroarenes and cumarins with diazonium salts (oxidative quenching) (Scheme 1c).



Scheme 1. Porphyrins as photoredox catalysts in C-C bond forming reactions