HIGHLY REDUCING ORGANIC PHOTOREDOX CATALYSTS AND THEIR APPLICATION TO FLUOROALKYLATION OF OLEFINS

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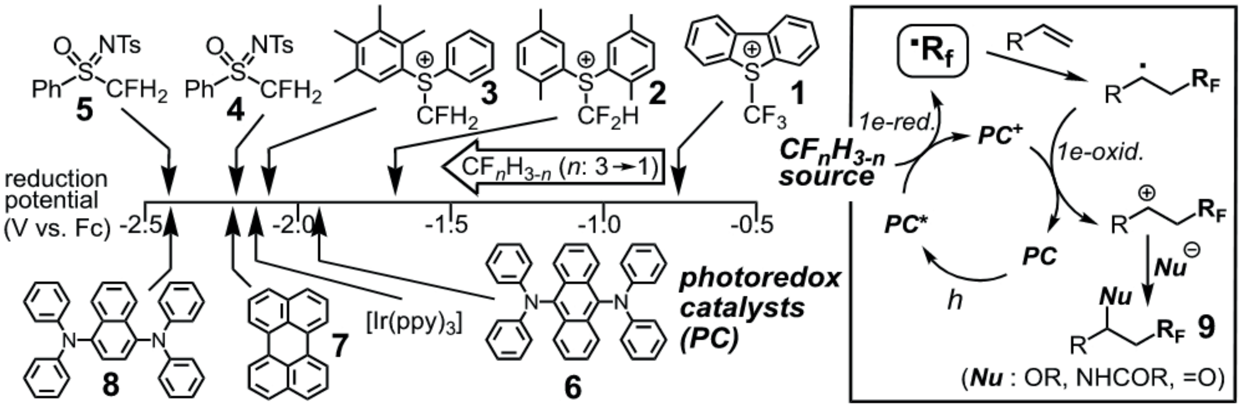
Fluoroalkyl groups (R_f) such as CF_nH_{3-n} groups are versatile structural motifs, especially in the fields of pharmaceuticals and agrochemicals, and development of simple methodologies for efficient and selective incorporation thereof into various organic skeletons is therefore highly demanded. On the other hand, photoredox catalysis via radical interediates[1] has attracted increasing attention as *a practical, green synthetic chemical process, because it is promoted by visible light including sunlight. Herein we will present various fluoroalkylations of olefins promoted by highly reducing organic photoredox catalysts.*

Cationic trifluoromethylating reagents such as Umemoto's reagent 1 turn out to be excellent CF_3 radical sources upon 1e-reduction by the action of photoredox catalysis ($PC^* \rightarrow PC^+ + 1e^-$).[2] But replacement of the most electron-withdrawing fluorine atom by a hydrogen atom (2, 3) causes significant negative shifts of the reduction potential. In addition, neutral precursors (4, 5) are more difficult to be reduced compared to the cationic ones, as readily anticipated. In order to expand the scope of not only fluoroalkylation via Rf radicals but also photoredox catalysis it has been demanded to develop highly reducing photoredox catalysts.



Taking into account this situation we developed highly reducing polyaromatic hydrocarbon catalysts 6 - 8, which were (1) even stronger than fac-[Ir(ppy)3] and (2) effective for various fluoroalkylative difunctionalization of olefins giving 9.[3]

References
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