Oxidative Aliphatic C-H Fluorination with Fluoride Ion Catalyzed by a Manganese Porphyrin

Scientific Achievement
A novel manganese-catalyzed fluorination process has been discovered that selectively fluorinates sp³ carbon-hydrogen bonds in alkanes, terpenoids and simple steroids by using simple fluorides as the fluorine source.

Significance and Impact
Carbon-fluorine bonds are emerging as increasingly important constituents of drugs, agrochemicals, and PET tracers. The reported manganese porphyrin catalysts provide proof-of-concept for a new approach that transfers fluoride ions to a range of hydrocarbons in conjunction with a hypervalent iodine-based oxidant.

Research Details
- Direct formation of C-F bonds from strong C-H bonds. The new fluorination system can be applied to a variety of alkanes, terpenoids and steroids.
- Mechanistic studies implicate a unique manganese (IV) difluoride intermediate that fluorinates alkyl radicals generated by an oxomanganese complex.
- Density functional theory calculations predicted that coordination of fluoride on the manganese center plays a vital role in the fluorine transfer step.