

**Grammaticakis-Neumann Award Lecture 2017: Excited State Proton-Coupled Electron Transfer in Organic Synthesis**R. R. Knowles<sup>1</sup><sup>1</sup>Department of Chemistry, Princeton University, Princeton, USA - rknowles@princeton.edu

Proton-coupled electron transfers (PCETs) are unconventional redox processes in which an electron and proton are exchanged together in a concerted elementary step. While PCET is now recognized to play a central role in biological redox catalysis and inorganic solar energy conversion technologies, its applications in organic chemistry remain largely unexplored. This talk will highlight our group's efforts to use photo-initiated PCET as a means to address significant and long-standing synthetic challenges in the areas of free radical chemistry and asymmetric catalysis. In particular we are interested in the ability of excited state PCET to enable catalytic and chemoselective generation of synthetically useful radical intermediates via the direct homolytic activation of common organic functional groups that are energetically inaccessible using conventional H-atom transfer catalysts. Our approach makes use of a simple thermodynamic formalism to rationally identify combinations of proton and electron donors that can formally transfer hydrogen to form very weak bonds (BDFEs <25 kcal/mol) and combinations of proton and electron acceptors that are competent to homolyze strong bonds (BDFEs >105 kcal/mol). Application of these concepts in the development of new synthetic methods will be presented.