Organophotocatalytic Dyads Tame Transient Radical Couplings

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Molecular organic dyads consisting of linked Donor-Acceptor (D-A) moieties find numerous applications as optical and light-harvesting devices.[1] Upon photoexcitation, charge transfer or formal charge separation (CT) can be advantageous or parasitic depending on the target application. Building on previous learnings on pre-assembling electrogenerated radical cationic and anionic photocatalysts,[2,3] this talk exemplifies how CT or CS states can be leveraged to pre-assemble electronically-complementary reaction partners. Upon photoexcitation of the resulting CT or CS states, transient radicals – that would otherwise undergo synthetically useless defunctionalizations / polymerizations – are generated and react in close proximity for synthetically useful couplings.[4] This demonstrates a conceptual metal-free alternative to transition metal catalysis for intercepting transient radical intermediates, and demonstrates the key importance of aggregation effects in photochemistry often overlooked by synthetic chemists.[5]

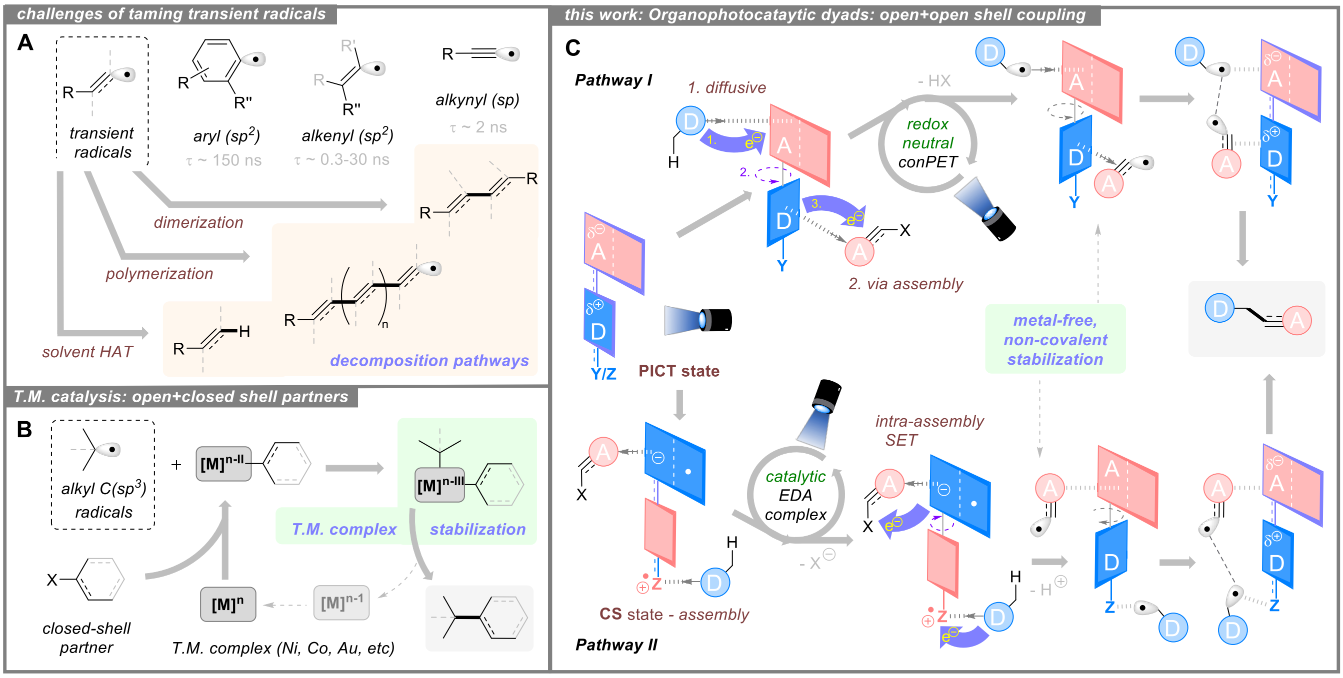

Figure 1. A. Properties and fates of transient radicals. **B.** Transition metal interception of transient radicals for couplings. **C:** Photocatalytic dyads - modes for generation / interception of radicals for couplings.

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