The Precision Photochemistry Paradigm

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Over the last decade our laboratory has employed monochromatic tunable laser systems to reveal a strong mismatch between the absorptivity of a chromophore and its photochemical reactivity in the vast majority of covalent bond forming reaction as well as specific bond cleavage reactions. Our data overturns the long-held paradigm that effective photochemical reactions are obtained in situations where there is strong overlap between the absorption spectrum and the emission wavelength under a given set of reaction conditions. However – as we explore herein – the absorption spectrum of a molecule provides only information about singlet excitation and remains largely silent on the accessibility of the critical triplet states, which dictate photochemical reactivity. We propose future avenues of enquiry on how photochemical action plots can be understood and demonstrate how they are of key importance for tailoring photochemical applications in soft matter materials design – including in advanced 3D printing and photoresponsive macromolecular systems – with never before seen precision, exploiting wavelength orthogonal, synergistic, cooperative and antagonistic photochemical reaction modes.

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