Photophysics of Perylene Diimide Dianions and Their Application in Photoredox Catalysis

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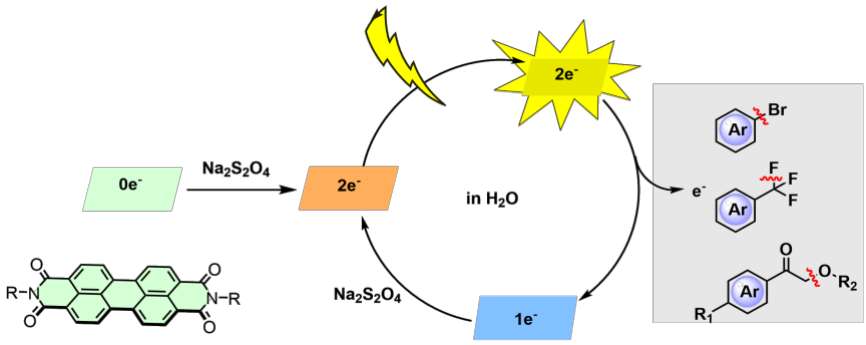
The two-electron reduced forms of perylene diimides (PDIs) are luminescent closed-shell species whose photochemical properties seem underexplored. We report here an in-depth optical spectroscopic study of several PDI^{2-} derivatives in both organic solvent and water. Furthermore, we disclose the usage of a PDI^{2-} for the photocatalysis of organic reactions, both in neat water and in water-acetonitrile mixtures using a phase transfer reagent as co-catalyst.



Our proof-of-concept study demonstrates that straightforward (single) excitation of PDI dianions with green photons provides an excited state that is similarly or more reducing than the much shorter-lived excited states of PDI radical monoanions ($PDI^{\bullet-}$), which are typically accessible after biphotonic excitation with blue photons. Thermodynamically demanding photocatalytic reductive dehalogenations and reductive C–O bond cleavage reactions of lignin model compounds have been performed using sodium dithionite ($Na_2S_2O_4$) acts as a reductant, either in aqueous solution or in biphasic water–acetonitrile mixtures in the presence of a phase transfer reagent. Our work illustrates the concept of multi-electron reduction of a photocatalyst by a sacrificial reagent prior to irradiation with low-energy photons as a means of generating very reactive excited states.

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