

Redox–protonation landscape of indene-annulated perylenes: chemodivergent switching of multistate NIR chromophores

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Streszczenie

Indene-annulated perylenes merge cyclopentadiene-like benzylic acidity with the multielectron redox chemistry of rylene carbonyl scaffolds, creating discrete redox–protonation (“Pourbaix”) spaces in which electron transfer and acid–base processes become intrinsically coupled. Here we map the accessible states of doubly and singly pentannulated perylenediimides and perylene tetraesters using absorption/emission spectroscopy, electrochemistry and spectroelectrochemistry, and DFT analysis. Voltammograms of all derivatives show two quasi-reversible, largely core-centered reductions, yet the pentannulated tetraesters uniquely undergo electrochemically induced γ -deprotonation prior to core reduction, consistent with electrogenerated-base chemistry. Chemical stimulation reveals pronounced chemodivergence: potassium *tert*-butoxide readily produces deprotonated “dienolate” NIR chromophores in the pentannulated tetraester series, whereas the corresponding diimides first form perylene-centered radical anions/dianions that evolve into benzylic anions and higher multianions in a cation-dependent manner, with crown ether sequestering K^+ and reshaping reaction trajectories. Strong reductants enable entry into highly reduced charge states, including an X-ray-verified salt of a pentannulated diimide trianion displaying diverse potassium binding motifs, underscoring the non-innocent role of ion pairing. Oxidation of deprotonated dianions furnishes weakly coupled neutral diradicaloids with NIR absorption. These results establish indene-annulated rylenes as multistate NIR chromophores whose experimentally accessible Pourbaix subsets can be programmed by redox bias, base strength, and cation coordination, with direct implications for organic electrochromism and rylene-based energy-storage chemistries.

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