

Phosphine Oxide-Functionalized Terthiophene Redox SystemsD. Käch¹, A. C. Gasser¹, L. Wettstein¹, C. Schweinzer¹, M. J. Bezdek^{1*}¹Department of Chemistry and Applied Biosciences, ETH Zurich

Redox systems based on main group elements are emerging as next-generation building blocks for organic batteries, electrochromic materials, magnets, photovoltaics, and sensors.^[1] Although they are attractive from economic and sustainability perspectives,^[2] main group elements typically feature a lower density of redox states compared to transition metals and consequently yield difficult-to-control, highly reactive radical species upon electron transfer.^[3] Despite their reactivity, main group redox systems could prove especially valuable in energy storage devices as chargeable electrolytes. In particular, oligothiophenes, one of the most widely studied structural motifs in organic electronics,^[4] offer the possibility of multi-electron storage at extremely negative potentials. However, studies on the electrochemical reduction of oligothiophenes have established the instability of the formed anions upon charging.

Here, we present our finding that diarylphosphine oxide functionalization of terthiophenes stabilizes their respective anions formed upon reduction. A crystalline phosphine oxide-functionalized terthiophene radical anion was synthesized wherein the redox-responsive nature of the platform was established using combined structural, spectroscopic, and computational characterization. Structural modification led to the identification of a variant that exhibits exceptional stability during bulk two-electron galvanostatic charge-discharge cycling, indicating that phosphine-oxide functionalized terthiophenes could be a promising new class of main group electrolytes for energy storage applications.^[5]

[1] Thomas Baumgartner, Frieder Jaekle *Main Group Strategies towards Functional Hybrid Materials*, Wiley, New York, **2018**.

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[3] Philip P. Power, *Chem. Rev.* **2003**, *103*, 789–810.

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[5] Daniel Käch, Aurelio C. Gasser, Lionel Wettstein, Clara Schweinzer, Máté J. Bezdek, *Angew. Chem. Int. Ed.* **2023**, e202304600.