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Conformational Flexibility of Xanthene-based Covalently-linked Dimers MARIJA ZORIC, USHA PANDEY KADEL, KSENIJA GLUSAC, Bowling Green State University — Our group investigated metal-free molecules that accelerate oxidation of water to molecular oxygen. One avenue of our research involves an investigation of the iminium and oxonium ion dimers ($2R^+$) as potential water oxidation electrocatalysts based on 3 catalytic steps: (1) $2R^+ + 2H_2O \rightarrow 2ROH + 2H^+$; (2) $2ROH \rightarrow RO-OR + 2H^+ + 2e^-$; (3) $RO-OR \rightarrow R^+-R^+ + O_2 + 2e^-$. The second step of the catalytic cycle involves the oxidation of two ROH alcohol units to generate the peroxide RO-OR. The relative geometry of the 2 monomer units is essential for efficient formation of the weak peroxide bond. In search for an ideally suited covalent linker that brings two ROH monomer units into the desired relative orientation, we studied conformational flexibility of 3 covalently-linker dimers (CLDs) consisting of two xanthene-based moieties connected by a diphenyl ether (DPE), 9,9-dimethylxanthene (Xan) or biphenyl (biph) as a linker. The study employs NMR spectroscopy, X-ray crystallography, and DFT calculations. As each dimer exhibits conformational degrees of freedom associated with rotations of the xanthene moiety, three different conformations are possible: *In_in*, *In_out* and *Out_out*, but only *In_in* is desirable for catalysis. While DPE(OH)₂ and Xan₃(OH)₂ have *In_out* conformation in solid state, biph(OH)₂ exist as *In_in* conformer. Solution studies show that DPE(OH)₂ freely rotate on NMR timescale, but Xan₃(OH)₂ and biph(OH)₂ are locked in *In_in* conformer.

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