

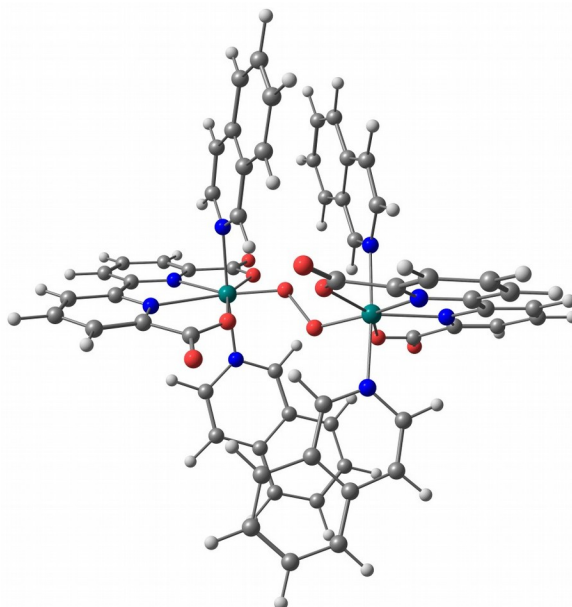
# IMPROVING RUTHENIUM-BASED WATER SPLITTING

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Rational design of artificial water-splitting catalysts is central for developing new sustainable energy technology. The catalytic efficiency of the natural water-splitting enzyme, photosystem II, has been remarkably difficult to achieve artificially; only recently have synthetic, molecular catalysts with comparable activities been presented.<sup>[1]</sup> Here, using powerful first-principles quantum chemical reaction path calculations and hybrid quantum mechanics/classical mechanics (QM/MM) simulations, we explore the elusive molecular mechanism of a class of ruthenium-based catalysts. We find that the thermodynamic driving force for the water-splitting process is obtained from the free energy released from  $\pi$ -stacking interactions within the catalytically active dimer core. Understanding the reaction mechanism allows us to design new catalysts that further lower the activation barrier for the water-splitting process by systematically increasing weak interactions within the catalytic dimer.<sup>[2]</sup>

1) L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun. A molecular ruthenium catalyst with water-oxidation activity comparable to that of photosystem II. *Nat. Chem.* **2012**, *4*, 418–423.

2) M.P. Johansson, V.R.I. Kaila, *practically submitted manuscript*