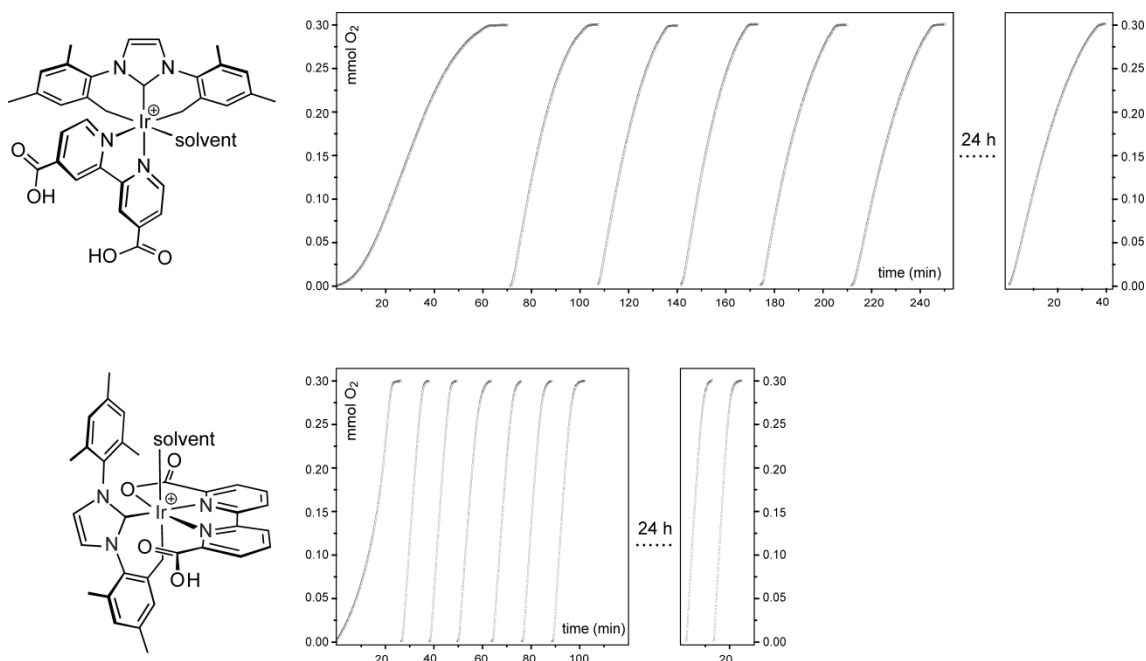


OXYGEN EVOLVING [Ir(IMes'')] COMPLEXES

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The cationic fragment $[\text{Ir}(\text{IMes}'')]^+$, which contains a doubly cyclometalated IMes ligand [1], has been used to prepare water-soluble complexes that catalyze the production of oxygen from periodate and water [2]. Catalyst solubility in water is achieved using bipyridine (bipy) auxiliary ligands that contain deprotonable carboxylic groups, whose positions in the bipy skeletons determine both the speciation in aqueous solution and the catalytic activities. Thus, the ligands with carboxylic substituents in positions 4,4' (above in the figure) or 6,6' (below) lead to different main species and, once deprotonated, give rise to catalytic profiles evidencing different activities and rate dependences on periodate concentration.



The catalysts need to be activated in the presence of excess periodate and, preferably, visible light, and after activation they become virtually immortal. They can maintain remarkable turnover frequencies, above 3.5 s^{-1} at 30°C , during months and after thousands of turnovers, as exemplified in the picture, in which every separate run corresponds to the evolution of 1200 molecules of oxygen per molecule of the catalysts.

The molecular nature of the catalysts and the likely source of the oxygen atoms (water or periodate) will be discussed on the basis of analytic, spectroscopic and kinetic experimental information.

References

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 [2] J. M. Thomsen, D. L. Huang, R. H. Crabtree, G. W. Brudvig, *Dalton Trans.*, **2015**, *44*, 12452-12472.