Bipyridine Covalent Triazine Framework beyond a Catalyst Support for an Iridium Complex: Elucidating the Promotional Role of Support in Aerobic Oxidation Catalysis

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The research for creating synergistic systems in heterogeneous catalysis displaying superior catalytic performances even better than the homogeneous analogs is indispensable for the development of industrial processes. The past decade has testified continuous attempts for the development of heterogeneous catalysts representing promotional performances. The majority of these examples include bimetallic catalyst systems in which the two promoter elements display synergistic benefits compared to their monometallic homogeneous and heterogeneous counterparts. However, the use of metal catalysts inescapably raises the cost of preparation and the environmental issues. Herein, we discovered an impressive performance of a covalent triazine framework based on bipyridine building blocks serving as an unusual promoter in the oxidation reactions. We demonstrate that bipy-CTF as support can significantly boost the efficiency of a half-sandwich $Ir^{III}Cp^*$ (Cp*= pentamethylcyclopentadienyl) complex giving a heterogeneous catalyst that outperforms its homogeneous counterpart. We report a mechanistic study to provide insights into the function of the Ir complex, bipy-CTF as well as the synergistic effect. The electron paramagnetic resonance (EPR) and in-situ XANES analyses provide strong evidences of the reaction mechanism proving the applicability of bipy-CTF to activate oxygen and alcohols and further enhancing the performance of the Ir complex. To the best of our knowledge, this is not only an unprecedented report on promoting the activity of a heterogeneous catalyst through a solid support but also the first report on the applicability of CTFs providing activated oxygen and substrate that is a key step in oxidation reactions.