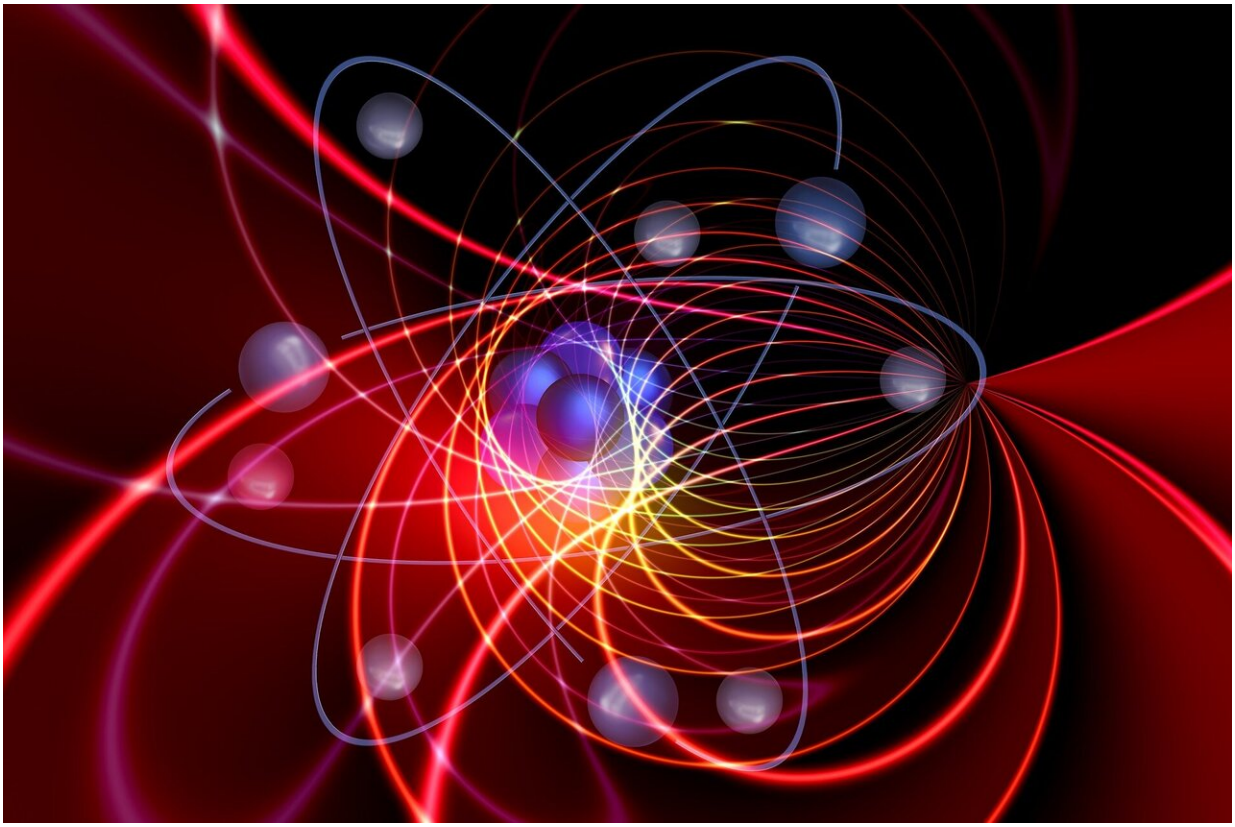
Scientists realize concerted four-electron reduction of nitrosobenzene

November 26 2021



Credit: Pixabay/CC0 Public Domain

Nitrosobenzene (PhNO) is implicated in a range of chemical transformations. A plethora of transition metal complexes can activate PhNO in various coordination modes, and electron-rich low-valent metal

centers can induce reduction of PhNO.

However, the functionalization of PhNO through the synergistic interaction of metal and ligand is still unclear.

Recently, Prof. Ye Shengfa's group from the Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences (CAS), in collaboration with Prof. Qu Jingping's group from Dalian University of Technology, achieved facile conversion of nitrosobenzene to aniline under ambient conditions by a thiolate-bridged diiron complex.

This study was published in *Journal of the American Chemical Society* on Oct. 7.

By using X-ray single crystal diffraction, 57Fe Mössbauer nuclear magnetic resonance, and infrared spectroscopies coupled with density functional theory calculations, the researchers proposed an unprecedented activation pathway of PhNO induced by a thiolate-bridged diiron complex.

Such a transformation realized concerted yet asynchronous four-electron reduction of PhNO to selectively furnish benzenesulfinamide, for which the four electrons all came from the bridging thiolate ligand, whereas the iron center only served as an electron shuttle. The resulting sulfinamide ligand had a greater propensity to undergo further reduction to release aniline compared with PhNO.

"The formation of sulfinamide accelerates degradation of PhNO to aniline, which helps to understand the metabolism of PhNO in biological systems," said Prof. ye.

More information: Sunlin Xu et al, Generation of a Sulfinamide Species from Facile N–O Bond Cleavage of Nitrosobenzene by a

Thiolate-Bridged Diiron Complex, *Journal of the American Chemical Society* (2021). DOI: 10.1021/jacs.1c03542