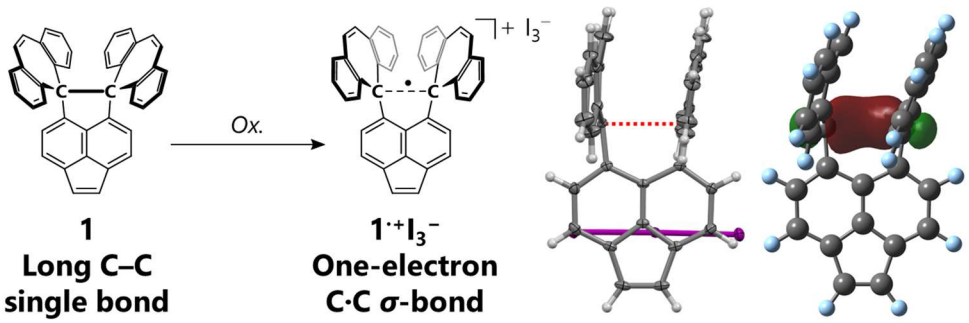
Exploring the ultimate covalent bond based on carbon

(*Graduate School of Science, The University of Tokyo*) ○Takuya Shimajiri
Keywords: One-electron C•C σ-bond; X-ray analysis; Raman spectroscopy; Near-infrared absorption

Covalent bonds share electron pairs between two atoms and make up the skeletons of most organic compounds in single, double and triple bonds. Meanwhile, Pauling proposed a concept of covalent bonds with one unpaired electron ('one-electron σ-bonds') in 1931, which is shared between two atoms.[1] In striking contrast to the large body of work on electron-pair bonds, the paucity of examples with one-electron bonds is remarkable, which is most likely due to their intrinsic weakness. So far, merely five studies have reported on the subject of one-electron bonds between atoms other than carbon.[2-5] Importantly, since Pauling's postulation almost a century ago, direct evidence (*e.g.*, X-ray structural analysis) that would corroborate the presence of such one-electron bonds between carbon atoms, which is arguably the most prevalent element in organic chemistry, has remained recalcitrantly elusive. Although several attempts have been made to directly prove the presence of a one-electron bond, in almost all cases these one-electron bonded species were only detected transiently using methods such as electron-spin-resonance.

In this work, the isolation of a compound with a one-electron σ-bond between carbon atoms is reported by means of the one-electron oxidation of a HPE-type hydrocarbon with an elongated C–C single bond.[6] The presence of the C•C one-electron σ-bond (2.921(3) Å at 100 K) was confirmed experimentally by single-crystal X-ray diffraction analysis and Raman spectroscopy for the single crystals of the obtained salt, and theoretically by density functional theory calculations.



1) L. Pauling, *J. Am. Chem. Soc.* **1931**, *53*, 3225.; 2) G. Bertrand *et al., Science* **1998**, *279*, 2080.; 3) J. C. Peters *et al., J. Am. Chem. Soc.* **2013**, *135*, 3792.; 4) M. Wagner *et al., Angew. Chem. Int. Ed.* **2014**, *53,* 4832. 5) J. Xie, J.-H. Su, X.-J. Yang *et al., J. Am. Chem. Soc.* **2024**, *146*, 2333–2338.; 6) T. Shimajiri, S. Kawaguchi, T.Suzuki, Y. Ishigaki, *Nature* **2024**, *634*, 347-351.