The iron sulfide proteins in nature are represented by those consisting of [4Fe-4S], [3Fe-4S], and [2Fe-2S] clusters. In most of the cases, these clusters are stable, and the core geometries are readily synthesized by spontaneous self-assembly reactions in polar aprotic solvents. We have recently found a new methodology to construct Fe sulfide clusters, which utilizes the bis-amide complex of iron, Fe\{N(SiMe$_3$)$_2$\}_2, as the precursor. This new route has allowed us to build iron/sulfide clusters in non-polar solvents, and resulted in a series of unprecedented cluster structures, some of which resemble closely the active sites of nitrogenases.

The unusual [8Fe-7S] inorganic core structure of the reduced form of P-cluster (P$^\text{N}$) was self-assembled by the reaction of Fe\{N(SiMe$_3$)$_2$\}_2, tetramethylthiourea (tmtu), 2, 4, 6-triisopropylbenzenethiol (HS-tip), and elemental sulfur in the ratio of 8(Fe):3(tmtu):12(HS-tip):7(S). Interestingly the complex [{N(SiMe$_3$)$_2$}\{SC(NMe$_2$)$_2$\}Fe$_4$S$_3$\{µ$_6$-S\}{µ-N(SiMe$_3$)}$_2$]$_2$. (1), obtained therefrom, consists of irons with a 6Fe(II)+2Fe(III) oxidation state as manifested by the Mössbauer study, while P$^\text{N}$ has been thought to carry 8 Fe(II) ions. Although cluster 1 degrades to a Fe$_4$S$_4$ cubane cluster under the presence of thiols, as the P-cluster does so, it was possible to synthesize (NEt$_4$)$_2$[{N(SiMe$_3$)$_2$}\{SAr\}Fe$_4$S$_3$\{µ$_6$-S\}{µ-N(SiMe$_3$)}$_2$ \(\times 2\) (Ar = 4-''Bu-C$_6$H$_4$, 2-SiMe$_3$-C$_6$H$_4$ etc.) from the reactions of 1 with corresponding ammonium salts of thiolates. We have also isolated [(S-dmp)Fe$_4$S$_3$\{µ$_6$-S\}(µ-S-dmp)$_2$\{µ-N(SiMe$_3$)}] \(\times 3\) from the reaction of Fe\{N(SiMe$_3$)$_2$\}_2, HS-dmp, HS-tip, and elemental sulfur (8:6:10:7), which is topologically analogous to FeMo-co and has an intriguing 5Fe(II)+3Fe(III) oxidation state.