

Elevated Reductive Defluorination of Branched Per and Polyfluoroalkyl Substances by Soluble Metal-Porphyrins and New Mechanistic Insights on the Degradation

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Abstract : Reductive defluorination has emerged as a sustainable approach to clean water from Per and polyfluoroalkyl substances (PFASs), also known as forever organic containments. For last few decades, nano zero valent metals (nZVMs) have been intensively applied in the reductive remediation of groundwater contaminated with chlorinated organic compounds due to its low redox potential, easy application, and low production cost. However, there is inadequate information on the effective reductive defluorination of linear or branched PFAS using nZVMs as reductants because of the lack of suitable catalysts. CoII-5,10,15,20-Tetraphenyl-21H,23H-porphyrin (CoTPP) has been recently reported for effective catalyzing reductive defluorination of branched (br-) perfluorooctane sulfonate (PFOS) by using TiIII citrate as reductant. However, the low water solubility of CoTPP limited its applicability. Here, we explored a series of structurally related soluble cobalt porphyrin catalysts based on our previously reported best performing CoTPP. All soluble porphyrins [[meso-tetra(4-carboxyphenyl)porphyrinato]cobalt(III)]Cl·7H₂O (CoTCCP), [[meso-tetra(4-sulfonatophenyl) porphyrinato]cobalt(III)]·9H₂O (CoTSPS), and [[meso-tetra(4-N-methylpyridyl) porphyrinato]cobalt(II)](I)₄·4H₂O (CoTMpyP) displayed better defluorination efficiencies than CoTPP. Especially, CoTMpyP presented the best defluorination efficiency for br-PFOS (94 %), branched perfluorooctanoic acid (PFOA) (89 %), and 3,7-Perfluorodecanoic acid (PFDA) (60 %) after 1 day at 70 °C. CoTMpyP-nZn0 system showed 88-164 times higher defluorination rate than VB12-nZn0 system in terms of all investigated br-PFASs. The CoTMpyP-nZn0 also performed effectively at room temperature, demonstrating the potential prospect for in-situ reductive systems. Based on the analysis of the intermediate products, the calculated bond dissociation energies (BDEs) and possible first interaction between CoTMpyP and PFAS, degradation pathways of 3,7-PFDA and 6-PFOS are proposed.

Keywords : cationic, soluble porphyrin, cobalt, vitamin b12, pfas, reductive defluorination

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