Toward iron sensors: bioinspired tripods based on fluorescent phenol-oxazoline coordination sites.

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In the quest for fast throughput metal biosensors, it would be of interest to prepare fluorophoric ligands with surface-adhesive moieties. Biomimetic analogues to microbial siderophores possessing such ligands offer attractive model compounds and new opportunities to meet this challenge. The design, synthesis, and physicochemical characterization of biomimetic analogues of microbial siderophores from *Paracoccus denitrificans* and from the *Vibrio* genus are described. The (4*S*,5*S*)-2-(2-hydroxyphenyl)-5-methyl-4,5-dihydro-1,3-oxazole-4-carbonyl group ($\mathbf{L}^{\mathbf{a}}$), noted here as an HPO unit, was selected for its potential dual properties, serving as a selective iron(III) binder and simultaneously as a fluorophore. Three tripodal symmetric analogues *cis*-$\mathbf{L}^{\mathbf{b}}$, *cis*-$\mathbf{L}^{\mathbf{c}}$, and *trans*-$\mathbf{L}^{\mathbf{c}}$, which mainly differ in the length of the spacers between the central carbon anchor and the ligating sites, were synthesized. These ferric-carriers were built from a tetrahedral carbon as an anchor, symmetrically extended by three converging iron-binding chains, each bearing a terminal HPO. The fourth chain could contain a surface-adhesive function ($\mathbf{L}^{\mathbf{c}}$). A combination of absorption and emission spectrophotometry, potentiometry, electrospray mass spectrometry, and electrochemistry was used to fully characterize the corresponding ferric complexes and to determine their stability. The quenching mechanism is consistent with an intramolecular static process and is more efficient for the analogue with longer arms. Detection limits in the low nanogram per milliliter range, comparable with the best chemosensors based on natural peptide siderophores, have been determined. These results clearly demonstrate that these tris(phenol-oxazoline) ligands in a tripodal arrangement firmly bind iron(III). Due to their fluorescent properties, the coordination event can be easily monitored, while the fourth arm is available for surface-adhesive moieties. The tripodal system is therefore an ideal candidate for integration with solid-state materials for the development of chip-based devices and analytical methodologies.

Słowa kluczowe

Fluorescence, Iron, Ligands, Molecular structure, reaction mechanisms