

Synthesis of Fluorescent PET-Type “Turn-Off” Triazolyl Coumarin Based Chemosensors for the Sensitive and Selective Sensing of Fe⁺³ Ions in Aqueous Solutions

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Abstract : Environmental pollution by ionic species has been identified as one of the biggest challenges to the sustainable development of communities. The widespread use of organic and inorganic chemical products and the release of toxic chemical species from industrial waste have resulted in a need for advanced monitoring technologies for environment protection, remediation and restoration. Some of the disadvantages of conventional sensing methods include expensive instrumentation, well-controlled experimental conditions, time-consuming procedures and sometimes complicated sample preparation. On the contrary, the development of fluorescent chemosensors for biological and environmental detection of metal ions has attracted a great deal of attention due to their simplicity, high selectivity, eidetic recognition, rapid response and real-life monitoring. Coumarin derivatives S1 and S2 (Scheme 1) containing 1,2,3-triazole moieties at position -3- have been designed and synthesized from azide and alkyne derivatives by CuAAC “click” reactions for the detection of metal ions. These compounds displayed a strong preference for Fe³⁺ ions with complexation resulting in fluorescent quenching through photo-induced electron transfer (PET) by the “sphere of action” static quenching model. The tested metal ions included Cd²⁺, Pb²⁺, Ag⁺, Na⁺, Ca²⁺, Cr³⁺, Fe³⁺, Al³⁺, Cd²⁺, Ba²⁺, Cu²⁺, Co²⁺, Hg²⁺, Zn²⁺ and Ni²⁺. The detection limits of S1 and S2 were determined to be 4.1 and 5.1 uM, respectively. Compound S1 displayed the greatest selectivity towards Fe³⁺ in the presence of competing for metal cations. S1 could also be used for the detection of Fe³⁺ in a mixture of CH₃CN/H₂O. Binding stoichiometry between S1 and Fe³⁺ was determined by using both Jobs-plot and Benesi-Hildebrand analysis. The binding was shown to occur in a 1:1 ratio between the sensor and a metal cation. Reversibility studies between S1 and Fe³⁺ were conducted by using EDTA. The binding site of Fe³⁺ to S1 was determined by using ¹³C NMR and Molecular Modelling studies. Complexation was suggested to occur between the lone-pair of electrons from the coumarin-carbonyl and the triazole-carbon double bond.

Keywords : chemosensor, “click” chemistry, coumarin, fluorescence, static quenching, triazole

Conference Title : ICOC 2020 : International Conference on Organic Chemistry

Conference Location : Copenhagen, Denmark

Conference Dates : June 11-12, 2020