

Interwoven Hydrogen Bonding Donor–Acceptor Arrays Facilitate Fluorescence Turn-On Detection of Cyanide

Junyong Jo and Dongwhan Lee

Department of Chemistry, Indiana University, Bloomington, IN 47405

A xanthene-based chemical scaffold was structurally engineered to install guanidine and aldehyde functional groups that engage in remarkably strong intramolecular hydrogen bonding interactions. Restricted conformational flexibility of this key C=O···H–N motif is reflected on the slow exchange rate of the guanidine N–H protons and high C–N bond rotational barrier ($\Delta G^\ddagger = 10\text{--}16$ kcal mol⁻¹) observed even in polar solvent environment. An effective polarization of the C=O group by these N–H groups promotes the reactivity of the molecule toward nucleophilic cyanide ion. Notably, such reactivity-based recognition of CN⁻ is coupled to a significant (> 7-fold) enhancement in the fluorescence intensity ($\lambda_{\text{max}} = 440$ nm) in aqueous environment. The increased emission quantum yield (Φ_{F} ; from 2.4% to 17%) and fluorescence lifetime (τ ; from 0.37 ns to 2.57 ns) of the cyanide adduct can best be explained by changes in both radiative and non-radiative decay pathways upon chemical transformation of the fluorophore. In addition, a markedly decreased rate constant (> 60-fold) of the Boc-functionalized guanidine derivative provides significant insights into the functional role of hydrogen bonding in reactivity-based detection of CN⁻.