

Functionalized Azo Dyes to Detect Mercury in Water: Cooperative Interplay between Azo and Ethynyl Ligands

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Metal-induced chemical transformation of an azo dye was exploited for the colorimetric detection of mercury(II) ion in water. The addition of Hg(II) to an aqueous solution (pH = 7.4, HEPES buffer) of the probe resulted in a dramatic color change from yellow to colorless, with complete disappearance of the longer-wavelength absorption at 440 nm and concomitant development of new electronic transition at 350 nm. A combination of pH-dependent UV-vis measurements and $^1\text{H}/^{13}\text{C}$ NMR spectroscopic studies supported the notion that the functionally relevant form the probe molecule exists as the keto-hydrazone, rather than enol-azo, tautomer. A model compound which shares the same azo-based chromogenic unit but lacks the ethynyl tethers showed significantly slower response kinetics toward Hg(II). Mass spectrometric analysis of the reaction products is consistent with nucleophilic attack of OH^- on the hydrazone C=N double bond which is activated by coordination to Hg(II). This mechanistic model is further supported by increasing rate constants at higher pH. This molecular probe responds exclusively to μM -level Hg(II) ion in neutral aqueous solutions, whereas other common metal ions do not elicit any detectable color change.