

Metal-Based Luminescence Sensors for Gaseous Hormones

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Metal impregnated luminescent polymers are effective as ethylene sensors. Silver tetrafluoroborate (AgBF_4), when impregnated into the weakly luminescent polymer poly (vinyl phenyl ketone) (PVPK), rendered the otherwise inert polymer responsive to ethylene. Of the several ratios of AgBF_4 :PVPK that were investigated, only films containing a 2:1 ratio responded to ethylene with a consistent photoluminescence quench. The 2:1 film demonstrated two kinetic regimes in the quenching response: an initial, fast quench and a slower fading quench. After a conditioning process, in which the film was repeatedly exposed to ethylene and vacuum, the response consisted of only the rapid quench. The conditioned film response was proportional to ethylene pressure between 20 and 300 torr. Electron microscopy revealed the films to have an irregular morphology with islands of silver nucleation, which suggests that inhomogeneous sites may account for the different response regimes observed. The response is specific for gases that can serve as ligands to the impregnated metal ion, such as ethylene, propylene and ammonia, and to metal ions capable of binding these gases. Oxygen and water vapor do not inhibit the response of the silver-impregnated film to ethylene.

Luminescent Cu(I)-bis-phenanthroline complexes provide an alternate method for sensing small molecules. Through a ligand-facilitated redox reaction, the bulky complex $[\text{Cu}(\text{2,9-di-}t\text{-butyl-phenanthroline})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ can be readily prepared. This complex is highly emissive, with a remarkably long luminescence lifetime. The substantial bulk prevents close approach of the two ligands to the metal ion, and the average Cu(I)-N distances at 2.112 Å, 0.08 Å longer than in an unconstrained complex. Reaction with gaseous small molecule ligands, such as CO, results in a change in both the absorption and emission spectra consistent with displacement of one of the phenanthroline ligands. CO binding is reversible in solution, and occurs with a substantial quench in emission at 600 nm. Thus, $[\text{Cu}(\text{2,9-di-}t\text{-butyl-phenanthroline})_2][\text{B}(\text{C}_6\text{F}_5)_4]$ can serve as a solution phase sensor for CO and other similar small molecule ligands.