

ABSTRACT

DEVELOPMENT OF POLYPYRIDYL-LIKE MOLECULAR SENSORS

Colin Arlington Gyles

Optosensing studies were undertaken on seven (7) molecular systems: (1) di-2-pyridyl ketone 2-furoic acid hydrazone (dpkfah), (2) *fac*- $\text{Re}(\text{CO})_3(\text{dpknph})\text{Cl}$ (dpknph = di-2-pyridyl ketone *p*-nitrophenyl hydrazone), (3) $[\text{Ru}(\text{bpy})_2(\text{dpknph})]\text{Cl}_2$ (bpy = 2,2'-bipyridyl), (4) di-2-thienyl ketone *p*-nitrophenyl hydrazone (dsknph), (5) dpknph, (6) di-2-pyridyl ketone thiophene-2-carboxylic hydrazone (dpktch) and (7) *fac*- $\text{Mn}(\text{CO})_3(\text{dpknph})\text{Br}$. These polypyridyl-like hydrazones were conveniently synthesized, characterized, analyzed and shown to exhibit interesting physico-chemical properties and potential for use as chemical sensors for biomolecules (such as chemotactic N-formylamino acids and glucose) and environmentally important metal ions (such as cadmium and mercury).

Structural, optical and thermodynamic studies of dpkfah revealed the presence of hydrogen bonds in the solid state, reversible inter-conversion between two interlocked electronic absorption bands and use

of dpkfah as an optical sensor for a variety of chemical stimuli including Group 12 metal ions. Chemical stimuli in concentrations $< 1.00 \times 10^{-6} M$ can be detected and determined using dpkfah in non-aqueous media.

Optical measurements on *fac*-Re(CO)₃(dpknph)Cl in polar non-aqueous solvents revealed that the addition of NaBH₄ mark improvement in the optosensing properties of *fac*-Re(CO)₃(dpknph)Cl and allows N-formylamino acids in concentrations as low as $1.0 \times 10^{-5} M$ to be determined using the optical sensor *fac*-Re(CO)₃(dpknph)Cl in non-aqueous polar solvents.

Thermo-optical measurements on [Ru(bpy)₂(dpknph)]Cl₂ in DMSO showed that the equilibrium distribution of interlocked high- and low-energy electronic charge transfer bands is solvent and solute dependent controlled by the solvent-solute and solute-solute interactions. The interplay between the high-energy (α) and low-energy (β) conformations of [Ru(bpy)₂(dpknph)]Cl₂ allowed Group 12 metal ions in concentrations as low as $1.00 \times 10^{-8} M$ to be detected and determined using [Ru(bpy)₂(dpknph)]Cl₂ in DMSO in the presence and absence of NaBH₄.

Nuclear magnetic resonance studies on dsknph in non-aqueous solvents revealed sensitivity to solvent and temperature variations. Thermo-optical measurements on dsknph in DMSO confirmed the reversible inter-conversion between high- and low-energy electronic

absorption bands and allowed for the use of dsknph and surrounding solvent molecules as molecular sensors for Groups I and II metal ions.

Optical and thermo-optical measurements on the molecular sensors $[\text{Ru}(\text{bipy})_2(\text{dpknph})]\text{Cl}_2$, *fac*- $\text{Re}(\text{CO})_3(\text{dpknph})\text{Cl}$ and dpknph in the presence of monosaccharides revealed that monosaccharides can be detected and determined in concentrations 1×10^{-9} – 2×10^{-7} M. $[\text{Ru}(\text{bipy})_2(\text{dpknph})]\text{Cl}_2$ exhibited higher sensitivity toward glucose than did *fac*- $\text{Re}(\text{CO})_3(\text{dpknph})\text{Cl}$ and dpknph and showed more sensitive response to glucose than fructose.

The electronic absorption transitions of dpkch are sensitive to solvent, concentration, temperature and the presence or absence of substrates. Group 12 metal ions in concentrations as low as 1.00×10^{-6} M can be detected and determined using dpktch in DMSO. ^1H -NMR spectra of dpktch in different solvents and at different temperatures confirm the sensitivity of the amide proton to solvent and temperature variations.

Thermo-optical measurements on *fac*- $[\text{Mn}(\text{CO})_3(\text{dpknph})\text{Br}]$ in DMSO and DMF confirmed the presence and inter-conversion between low- and high-energy intra-ligand charge transfer transitions (ILCT). High values for the extinction coefficients and low values and sensitivity of the thermodynamic parameters, for the inter-conversion, to solution composition allowed for the use of this system (*fac*- $[\text{Mn}(\text{CO})_3(\text{dpknph})\text{Br}]$)

and surrounding solvent or solute molecules) as a spectrophotometric sensor for a variety of chemical stimuli that include metal ions. Group 12 metal ions in concentrations as low as $1.00 \times 10^{-9} \text{ M}$ can be detected and determined using *fac*-[Mn(CO)₃(dpknph)Br] in DMSO in the presence and absence of NaBH₄.