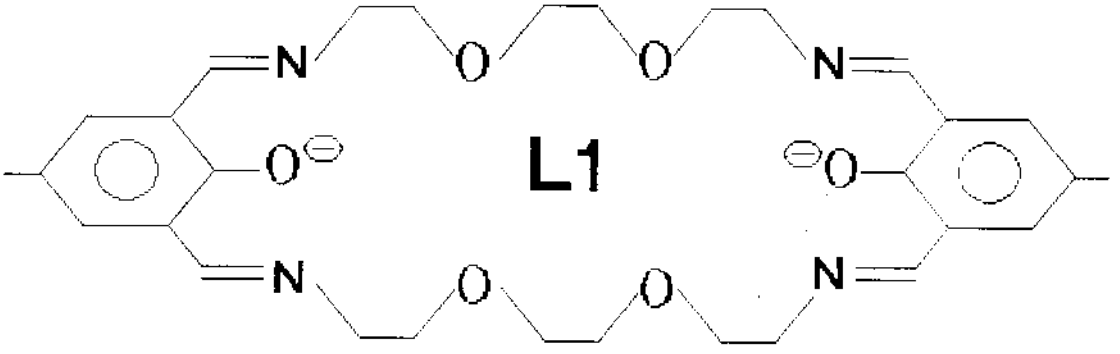
Abstract

Analytical tools for laser-induced luminescence and competitive complexation studies of supramolecular assemblies were developed and evaluated. A gas flow cryostat for variable temperature luminescence studies was also designed and built.

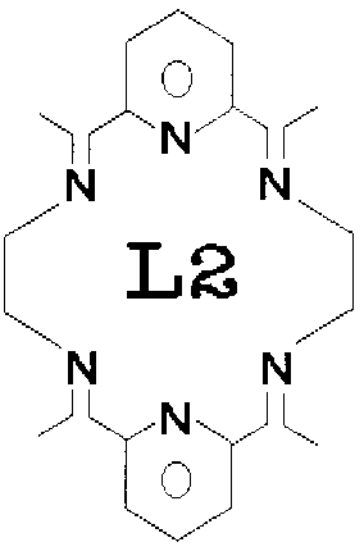
Molecular recognition in dinuclear lanthanide Schiff-base complexes of the ligand **L1** was subsequently studied and successfully modelled by a phase partitioning hypothesis. The selectivity of **L1** for lanthanide cations Ln_1 and Ln_2 was correlated to the cooperative effects of their ionic radii and perhaps atomic mass. The transfer of excitation energy between lanthanide cations in mixed-lanthanide complexes of **L1** was used to confirm the selective pairing of dissimilar cations within a single macrocycle.



Guest-host interactions in supramolecular assemblies of cubic F23 complexes with general stoichiometry $[(\mathbf{A}18\mathbf{C}6)_4(MnCl_4)_{1-x}(\mathbf{M}Cl_4)_x][\mathbf{Z}Cl_4]_2$ (**1AMZ** : **A** = Rb^+, Tl^+; **M** = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; **Z** = Tl^{3+}, Fe^{3+}) were studied. The relative thermodynamic stability trends of $\mathbf{M}Cl_4^{2-}$ anions was derived from the competitive complexation of MCl_4^{2-} species in the cubic lattice of **1AMZ** ; the stability sequence for **1AMZ** is $ZnCl_4^{2-}$ > $CoCl_4^{2-}$ > $CuCl_4^{2-}$ > $NiCl_4^{2-}$.

For complexes of **1RbMnTl** and **1TlMnTl**, the luminescence decay dynamics of $MnCl_4^{2-}$ ions in the cubic matrices revealed a thermally activated quenching mechanism. The activation energy was determined as ≈ 50 $kJmol^{-1}$ and the exciton traps were identified as water molecules presumably due to small amounts of **1AMnTl**·¼H_2O impurities. The luminescence decay of complexes with $CuCl_4^{2-}$ and $CoCl_4^{2-}$ substituted at $MnCl_4^{2-}$ sites in **1RbMnTl** revealed diffusive energy migration through the $[(Rb18\mathbf{C}6)_4MnCl]^{2+}$ sublattice. The coupling constants for electric dipole-dipole interactions in **1RbCuTl** are 2.4 x 10^{-40} m^6sec^{-1} for Mn-Cu energy transfer and 1.1 x 10^{-40} m^6sec^{-1} for Mn-Mn energy migration. Complexes of **1RbCoTl** provided Mn-Co and Mn-Mn coupling constants of 2.0 x 10^{-41} m^6sec^{-1} and 4.6 x 10^{-53} m^6sec^{-1} respectively.

In an attempt to extend the competitive complexation and luminescence decay kinetics methods to oligomeric systems, an oligomeric Schiff-base precursor to superconducting $YBa_2Cu_3O_{7-\delta}$ ceramics derived from 2,6-diacetylpyridine, ethylenediamine and yttrium, barium and copper nitrates was studied. The macrocyclic ligand **L2** was found to be the major component of the precursor system.



The thermal decomposition characteristics of the precursor were optimized and thick films of superconducting $YBa_2Cu_3O_{7-\delta}$ were subsequently prepared on ceramic magnesium oxide substrates.

Thorium substituted $Y_{1-x}Th_xBa_2Cu_3O_{7-\delta}$ ceramic powders with were also prepared by the Schiff-base precursor for relative concentrations of thorium up to 33% (x = 0.33).