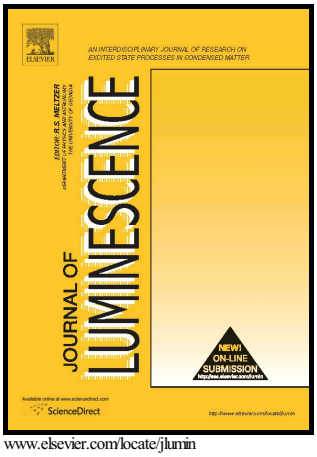

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A role of copper(II) ions in the enhancement of visible and near-infrared lanthanide(III) luminescence

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Abstract

Most of the existing optical methods for Cu^{II} detection rely on a "turn-off" approach using visible lanthanide(III) luminescence. In this work we present an innovative molecular systems where the podands bis(2-hydrazinocarbonylphenyl) ethers of ethylene glycol (L1) and diethylene glycol (L2) have been designed, synthesized and tested with an ultimate goal to create a "turn-on" lanthanide(III)-based molecular probe for the specific detection of Cu^{II} ions based on both visible (Tb^{III}, Eu^{III}) and near-infrared (Nd^{III}, Yb^{III}) emission. Quantum yields of the characteristic Ln^{III} emission signals increases by at least two-orders of magnitude upon addition of Cu^{II} into water/acetonitrile (9/1) solutions of LnL (L = L1, L2) complexes. A detailed investigation of ligand-centred photophysical properties of water/acetonitrile (9/1) solutions of CuL, GdL and GdCuL complexes revealed that the presence of Cu^{II} ions does not significantly affect the energy positions of the singlet (32 260 cm^{-1}) and triplet (25 640-25 970 cm^{-1}) states, but partially or fully eliminates the singlet state quenching through an electron transfer mechanism. This effect increases the probability of intersystem crossing leading to enhanced triplet-to-singlet emission ratio and to longer triplet state lifetimes. The redox activity of