



Research paper

Structural aspects, spectroscopic and third order nonlinear optical properties of mixed ligand complexes from NNO tridentate Schiff base: Crystal structure of a rare proton bridged Ni(II) complex

Manjari Jayendran^a, Sajin Ponnann^b, P.M. Sabura Begum^a, M.R. Prathapachandra Kurup^{a,c,*}

^a Department of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, Kerala, India

^b School of Physics, University of Hyderabad, Gachibowli, Hyderabad 500046, India

^c Department of Chemistry, School of Physical Sciences, Central University of Kerala, Tejaswini Hills, Periyar 671 316, India

ARTICLE INFO

Keywords:

Schiff base
Mixed ligand complexes
Proton bridged complex
Solvatochromism
Hirshfeld surface analysis
Third order nonlinear optical properties

ABSTRACT

Three novel mixed ligand complexes of cadmium(II), zinc(II) and nickel(II), derived from the parent Schiff base 4-chloro-2-((2-(dimethylamino)ethylimino)methyl)phenol, were synthesized and characterized by means of single crystal XRD, elemental analysis, IR, electronic and NMR spectral studies. In all the three complexes either reactant amine or aldehyde coordinates to the metal centers along with Schiff base and nickel(II) complex is having a rare proton bridged structure. While complex **1** crystallizes in orthorhombic *Pbca* space group, both complexes **2** and **3** crystallize in triclinic *P $\bar{1}$* space group. Different types of intermolecular interactions present in the crystal systems paved way to form 1D and 2D supramolecular assemblies and the visual analysis of those intermolecular interactions was achieved through Hirshfeld surface analysis. All the three complexes exhibited a negative solvatochromic behavior. Photoluminescent studies were carried out and quenching of fluorescence was observed in all complexes which is supported by the quantum yield values. Third order NLO properties were investigated by Z-scan technique with 75 fs laser pulse at 800 nm. NLO responses of the complexes were controlled by nonlinear refractive processes which make them suitable candidates for optical switching applications.

1. Introduction

Design and synthesis of transition metal complexes incorporating Schiff base ligands are of continuing interest in view of the possibility of obtaining diverse structures with intriguing properties. Schiff base metal complexes have been extensively studied in various fields of scientific research including catalysis [1], material science [2], optoelectronic applications [3], medicinal chemistry [4] etc. Synthetic versatility leading to diversity in structural topology is one of the key factors, which brings great deal of interest to Schiff base ligands in coordination chemistry. Moreover, their unique self-assembling nature, leading to the formation of various supramolecular architectures, have helped them to reach the status of privileged ligand platform [5]. Hydrogen bonding interactions together with weak non-covalent interactions, such as C–H... π , π – π , halogen bonding, unconventional hydrogen bonds *etc.*, are found to play a crucial role in forming diverse supramolecular patterns [6]. Also, the synthesis of mixed ligand complexes having aldehyde or amine as coligands is of significant importance, since they are having tremendous applications in the fields of

biochemistry [7,8] and analytical chemistry [9,10].

Transition metal complexes, especially Schiff base complexes, have emerged as promising candidates for the design and development of nonlinear optical (NLO) materials because of their efficient charge transfer behavior and ability to tailor metal-organic-ligand interactions [11]. Compared with the first generation of push-pull organic molecules, inorganic metal complexes offer a great structural diversity and improved tunable electronic and magnetic properties by virtue of central metal ion [12]. The origin of NLO responses is mainly due to the extensive π -delocalization within the molecule. Moreover, the introduction of electron donor/acceptor functionalities, which induce large asymmetry in electron density, enhance the responses too [13]. Herein, we have chosen a dimethyl substituted primary amine and chloro-substituted salicylaldehyde for the synthesis of Schiff base so as to obtain a D- π -A structure, where electron donor moiety (D) and electron acceptor moiety (A) are separated by a π -conjugated system. As the ligand coordinates to several transition metal ions in different oxidation states, NLO responses can be fine-tuned.

In the present endeavor, we report the synthesis and

* Corresponding author at: Department of Chemistry, School of Physical Sciences, Central University of Kerala, Tejaswini Hills, Periyar 671 316, India.
E-mail address: mrp@cukerala.ac.in (M.R.P. Kurup).

<https://doi.org/10.1016/j.ica.2019.118968>

Received 21 April 2019; Received in revised form 15 June 2019; Accepted 15 June 2019

Available online 17 June 2019

0020-1693/ © 2019 Elsevier B.V. All rights reserved.