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Structural Insights and Third Order NLO Studies of Pseudohalide- Based Polymeric and Monomeric Congeners of Halo-Substituted Parent Schiff Bases

Natarajan Aiswarya,^{*,[a]} Cheruvalath Ajina,^{*,[b]} Lincy Tom,^{*,[a]} and Maliyeckal R. Prathapachandra Kurup^{*,[a, c]}

The present work focuses on the pseudohalide embodied copper(II) complexes of a tridentate Schiff base (HL) derived from N,N-dimethylethylenediamine and 3,5-dichloro-2-hydroxyacetophenone. Of them, two are coordination polymers and rest are monomers. The azide in the complex $[Cu(L)(N_3)]_n$, adopts an *end-on* coordination mode begetting a *trans* helical propagation while the *end-to-end* bonding fashion of the dicyanamide in $[Cu(L)[N(CN)_2]]_n$ fostered a *meso*-helical chain. The interplay of covalent & non-covalent forces develop the complexes into supramolecular architectures. Similar forces stitch the monomeric cyanato and thiocyanato complexes to

chains. Quantification of intermolecular forces was achieved by surface analysis along with fingerprint plots. Charge-transfer bands exhibit negative solvatochromic effect while the influence of the solvents on the geometry of the complexes is based on *d-d* bands. Further, fluorescence and thermal studies were also done. The third order non-linear optical (NLO) response of the complexes were recorded. Open aperture scan showed a positive NLO absorption coefficient and closed scan, a negative non-linear refractive effect. A predominant refractive effect of the complexes make them ideal for optical switching applications.

Introduction

Unlike a synthetic organic chemist, who enjoys the luxury of a large number of reliable reactions at their disposal for preparing small molecules, coordination chemists with only a relatively few number of high-yielding reactions are always at a challenge. So as to surpass this, chemists are exploring ways to harness the directional bonding afforded by metal centers and the weak metal-ligand interactions in coordination complexes.^[1] An upsurge of publications in supramolecular chemistry in the last few decades corroborates the fact. The structure-activity relationship offered by Schiff bases make it a versatile ligand in coordination chemistry. Schiff base coordinated metal complexes are extensively used in the field of synthetic chemistry, supramolecular chemistry, material science, homogenous catal-

ysis, optoelectronic applications, biological chemistry as well as molecular magnetism, transport and separation phenomena.^[2] Design of energy materials based on metal Schiff base complexes are also witnessing an optimistic upswell in recent years.^[3] Arriving at a generalized synthetic procedure is rather tedious with so many factors like - the nature of metal ion, solvent, blocking organic ligand, metal:pseudohalide ratios *etc.*, controlling the nature of the final product.^[4]

One common strategy to build up di- and polynuclear transition metal complexes is the use of blocking ligands with lesser donor sites in combination with bridging ligands. Therefore, unsymmetrical Schiff base ligands with N, O or N donors along with various polydentate bridging anions have been able to produce diverse possibilities in structure as well as supramolecular architectures.^[5] The attributes like smaller length, rigidity and variety of coordination modes of donor atoms,^[6] make pseudohalides excellent bridging ligands for designing diverse topologies and frameworks. Although hydrogen bonding interactions are the protagonist non-covalent interaction for the supramolecular assembly, lone pair $\cdots\pi$, C-H $\cdots\pi$, cation $\cdots\pi$, anion $\cdots\pi$, halogen interactions and unconventional hydrogen bonds *etc.*^[7] also are responsible for the observed structural diversity.

In the present work, we have judiciously chosen a bisubstituted amine so as to deliberately suppress the hydrogen bonding capability of the resulting tridentate Schiff base thereby attempting to highlight the role of other weak interactions in the construction of supramolecular architectures.^[8a,b] Herein, we report a comprehensive study of the four copper complexes obtained from the same parent Schiff base, which differ only in the pseudohalide involved. Of the four

[a] Dr. N. Aiswarya, L. Tom, Prof. M. R. P. Kurup
Department of Applied Chemistry
Cochin University of Science and Technology
Kochi 682 022, Kerala, India
E-mail: ashier2007@gmail.com
lincyatomy123@gmail.com
mrp@cukerala.ac.in

[b] C. Ajina
International School of Photonics
Cochin University of Science and Technology
Kochi 682 022, Kerala, India
E-mail: ajinac25@gmail.com

[c] Prof. M. R. P. Kurup
Department of Chemistry, School of Physical Sciences
Central University of Kerala
Riverside Transit Campus
Nileshwar, 671 314, India

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