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Helical and network coordination polymers based on a novel C_2-symmetric ligand : SHG enhancement through specific metal coordination†

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Received (in Cambridge, UK) 6th January 2004, Accepted 20th February 2004
First published as an Advance Article on the web 25th March 2004

Cu(I) and Ag(I) coordination polymers of an axially chiral "push–pull" ligand possess respectively 2-D network and helical structures and the coordination mode strongly influences the solid state SHG reduction/enhancement with respect to the free ligand.

The flexibility and versatility inherent in coordination polymer design facilitates the realization of a variety of supramolecular organizations and a wide range of materials attributes such as electrical conductivity, magnetism and optical characteristics.[1] Nonlinear optical (NLO) properties[2] of organized molecular assemblies is one of the key targets of current investigations in materials chemistry. Appreciable thermal stability and optical transparency that can be achieved through a judicious choice of metal ions and ligands makes coordination polymers particularly attractive candidates for NLO applications.[3] Coordination of metal atoms has been shown to enhance the nonlinearity at the molecular[4] and bulk[5,6] levels. The possibility of fine-tuning the hyperpolarizability, β, at the molecular level is an important advantage for realizing quadratic effects such as second harmonic generation (SHG). A variety of metals such as Zn and Cd as well as transition elements like W, Ni, Cu and Ru and ligands based on Schiff bases, pyridines and stilbenes have been employed.[3,7–9] The quest for unravelling fundamental structure–property correlations in extended structures warrants the exploration of novel ligand–metal combinations that can lead to varied polymer architectures and facilitate the development of simple approaches to the interpretation of NLO characteristics.

Donor–acceptor substituted conjugated systems generally possess large β which can be enhanced further by the coordination of electropositive metals at the acceptor site. Considering this, and the fact that homochirality ensures the formation of noncentrosymmetric lattice structures, we have investigated the deployment of *N*,*N*′-bis(4-cyanophenyl)-(1*R*,2*R*)-diaminocyclohexane (BCDC)[10] as a novel C_2-symmetric ligand with a "push–pull" framework. The axial symmetry coupled with the multiple ligation sites of BCDC should allow the fabrication of different coordination polymer topologies. The optical transparency and the high probability of generating coordination polymers prompted the choice of Cu(I) and Ag(I) for complexation. We report the crystal structures and SHG capability of the free ligand as well as the two coordination polymers and analyze the interesting trends that they exhibit. The modes of coordination are strikingly different with the two metals leading to 2-D network and helical structures respectively. These novel materials demonstrate the critical role of the coordination mode and the polymer structure on the SHG.

BCDC was synthesized by the reaction of (1*R*,2*R*)-diaminocyclohexane with 4-fluorobenzonitrile.[10] Crystals grown by diffusion of hexane into ethyl acetate solution are found to belong to the $P2_12_12_1$ space group with one molecule in the asymmetric unit.[11]‡ A water molecule included in the unit leads to N–H···O ($r_{N7\cdots O25}$ = 3.035 Å, $\theta_{N7–H7\cdots O25}$ = 154.9°) and O–H···N ($r_{O25\cdots N24}$ = 2.999 Å, $\theta_{O25–H25A\cdots N24}$ = 122.7°) hydrogen bond bridges which together with direct N–H···N ($r_{N8\cdots N24}$ = 3.136 Å, $\theta_{N8–H8\cdots N24}$ = 161.8°) hydrogen bonds lead to an extended supramolecular network (Fig. 1). In contrast to the nitro analog BNDC,[12] BCDC does not form any helical superstructure. Layering a solution of BCDC in THF on top of a solution of $[Cu(CH_3CN)_4]PF_6$[13] in dichloromethane yielded crystals of $[Cu(BCDC)]PF_6$ at the interface. The crystals belong to the $P22_12_1$ space group with half the molecule and a molecule of THF in the asymmetric unit.[11] Cu(I) lies on a 2-fold axis and is tetrahedrally coordinated to the two amino nitrogens of BCDC and the cyano nitrogens of two other BCDC's leading to an extended 2-D network (Fig. 2).† The individual strands in the network have a zig-zag structure; no helical superstructure is observed. The coordination of the amino groups to Cu(I) is facilitated by the *exo* orientation of the cyanophenyl groups in BCDC. PF_6^- ions and THF appear in the channels of the network. Mixing acetone solutions of BCDC and $AgClO_4$ produced $[Ag(BCDC)]ClO_4$. Crystals grown by slow evaporation of acetonitrile solution are found to belong to the $P2_12_12_1$ space group with two molecules in the asymmetric unit.[11] Unlike the majority of known Ag(I)-cyano complexes,[14] the present one shows linear coordination of two cyano nitrogens around Ag(I). Significantly, the cyanophenyl groups in BCDC are now oriented *endo*, leading to a helical polymer chain formed through the Ag(I) links (Fig. 3).† The ClO_4^- ions reside in the helical channel. Both the Cu(I) and Ag(I) complexes are transparent (λ_{max} [$\lambda_{cut\text{-}off}$] = 362.2 [392.4] nm and 348.6 [367.8] nm respectively).

We have carried out Kurtz–Perry SHG measurements[15] on BCDC and the metal complexes; SHG variation with particle size indicates phase-matchable behavior in all cases. BCDC shows a

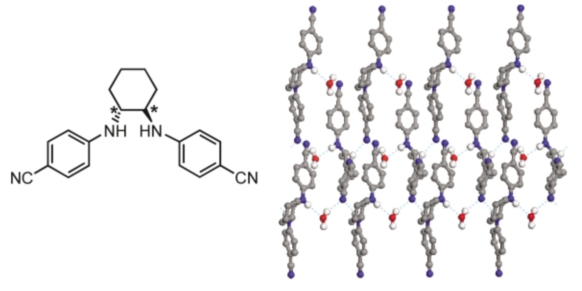

Fig. 1 Molecular structure of BCDC and packing in the BCDC·H_2O crystal; C (grey), N (blue), O (red), H (white); H-bonds (broken line).

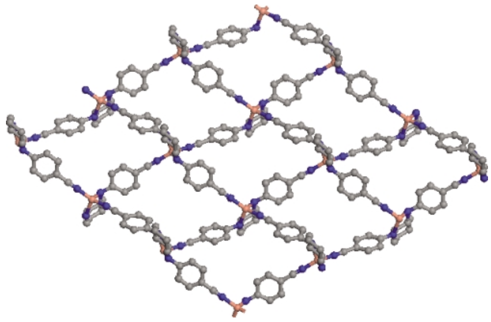

Fig. 2 2-D network structure in $[Cu(BCDC)]PF_6$·THF (*bc* plane); PF_6^- and THF are omitted for clarity; C (grey), N (blue) Cu (orange).

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† Electronic supplementary information (ESI) available: experimental, crystallographic and computational details. See http://www.rsc.org/suppdata/cc/b3/b316931f/

DOI: 10.1039/b316931f

moderate value saturating at 0.3 U (1 U = SHG of urea). Complexation of Cu(I) at the amino and cyano sites in [Cu(BCDC)]PF_6 leads to a small reduction in the SHG to 0.2 U. Interestingly, the complexation of Ag(I) at the cyano sites alone in [Ag(BCDC)]ClO_4 causes a nearly ten-fold increase in the SHG to 2.9 U; the SHG of some of the helical coordination polymers reported earlier[6,16] is ~1 U. The bulk SHG from materials is controlled by the molecular hyperpolarizability as well as the molecular organization. The impact of the molecular organization in the extended polymeric structure is difficult to quantify; the helical structure possibly enhances the bulk SHG.[12] The anion can influence the formation of the extended structures. However, investigation of the hexafluorophosphate and perchlorate salts of the Cu(I) complex and nitrate, acetate and perchlorate salts of the Ag(I) complex indicated that the SHG is largely independent of the anion. A simple computational approach provides insight into the influence of the conformation of BCDC and the coordination of the metal ion on the β. The conformation of the cyanophenyl groups in BCDC may be characterized by the torsion angle, τ(C_{phenyl}–N–C*–C*); the single crystal analysis shows that the τ are 157.9, 164.9 and 89.3° in BCDC, [Cu(BCDC)]PF_6 and [Ag(BCDC)]ClO_4 respectively, representing *exo*, *exo* and *endo* conformations. Previous studies[4] have employed semiempirical as well as *ab initio* methods to compute β. We have computed the static hyperpolarizability of these ligand structures using the AM1/TDHF[17] method; the geometries from crystal structure were used and H atom positions alone were optimized. The influence of the metal ions were assessed by placing point positive charges at the relevant sites (parameters for Ag(I) and Cu(I) are not available in this program). The computed β are collected in Table 1. The trends are in tune with classical push–pull concepts; they are further confirmed using *ab initio* computations[18] at the B3LYP/3-21G* level carried out on the same structures, but now with Cu(I) and Ag(I) metals in place. It is observed that the *endo* orientation of the phenyl rings leads to larger β. More significantly, the β is reduced by the coordination of Cu(I) at the cyano and amino groups whereas it is enhanced by coordination of Ag(I) at the cyano groups alone. Most notably, the computed β parallel the observed SHG values; the molecular nonlinearity appears to exert a dominant influence on the bulk property.

BCDC is shown to be a convenient ligand to fabricate fascinating coordination polymer topologies. The simple computational model provides meaningful insight into the trends of molecular nonlinearity in these polymeric systems and suggests a convenient approach to the design of coordination polymers for SHG applications.

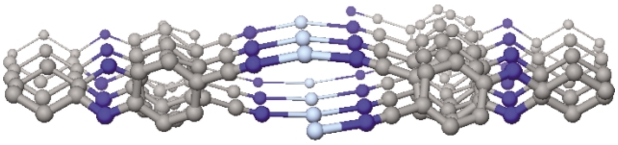

Fig. 3 Helical polymeric chain in [Ag(BCDC)]ClO_4 along the *b* axis; decrease of atom size schematically represents progression down the axis; ClO_4^- are omitted for clarity; C (grey), N (blue), Ag (cyan).

Table 1 Computed static hyperpolarizabilities of BCDC (in the free form and as ligands in the metal complexes) and the BCDC/metal systems; in the AM1 computations, the metal ions are replaced by point charges. Geometries are taken from the appropriate crystal structures with H atoms alone optimized in the AM1 method

Structure		β/esu AM1	β/esu B3LYP/3-21G*
BCDC	Ligand	7.49	4.74
[Cu(BCDC)]PF_6	Ligand	4.26	3.38
	Ligand/3Cu(I)[a]	3.85	1.49
[Ag(BCDC)]ClO_4	Ligand	9.66	6.53
	Ligand/2Ag(I)[b]	22.35	62.60

[a] Metal (charge) placed at the amino and the two cyano coordination sites.
[b] Metal (charge) placed at the two cyano coordination sites.

Financial support from DST, New Delhi (Swarnajayanti Fellowship) and the use of the National Single Crystal Diffractometer Facility (DST) at the School of Chemistry, University of Hyderabad are acknowledged with gratitude. SPA thanks the CSIR, New Delhi for a senior research fellowship.

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‡ CCDC 228200–228202. See http://www.rsc.org/suppdata/cc/b3/b316931f/ for crystallographic data in .cif format.

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