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Keywords: atomic polarizability, multipolar model, linear optic properties

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Charge-density studies of a new class of high performance NLO materials

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The current optoelectronics industry is highly motivated to finding new non-linear optical (NLO) materials since they are key to advanced display technologies, telecommunications and the laser industry. Organic NLO materials are attractive due to their large NLO response and fast response time. Despite the importance of the organic NLO chromophores, progress has been hampered by the incremental or serendipitous methods by which new classes of organic NLO materials have been discovered. Chance findings have had essentially random origins, while traditional NLO materials design methods are based on iterative chemical substitutions of an *a priori* known NLO active organic molecular framework. A new systematic approach to discover NLO materials was proposed by our group, which employs data-mining techniques combined with quantum mechanical calculations [1]. Two independent search strategies were implemented in this data-mining method, each predicting the best organic NLO materials and producing a ranked list of NLO response. Both approaches search a representative set of organic chemical space based on the Cambridge Structural Database (CSD). The CSD houses the world's repository of all published organic crystal structures. The backbone of 2,4,5,7-tetranitrofluorenes (TNFs) was one of the several promising structural motifs discovered in this prediction work and furthermore, their predicted NLO properties were among the highly-ranked. This study focuses on the experimental validation of the TNF derivatives.

TNFs are two-dimensional structures composed of *meta*-substituted strong electron-withdrawing nitro groups, connected to the fluorene backbone. Seven TNF derivatives with different electron-donating groups were studied here. Topological analysis of the molecular electronic structure and charge transfer dynamics were investigated by means of charge density studies: firstly, high resolution X-ray diffraction data were obtained from synchrotron-based diffractometer (BM01A, ESRF, France); secondly, complementary neutron diffraction was employed to locate the hydrogen positions and their hydrogen bonding network. Lastly, the neutron determined atomic positions and the scaled thermal factors for hydrogen were then used for the X-ray multipolar refinement. In order to compare the charge density analysis with the NLO response (hyperpolarizability, β), optical experiments based on hyper-Rayleigh scattering (HRS) technique [2] were carried out to characterise the absolute hyperpolarizabilities of the subject compounds.

The extended π-conjugation of the fluorene backbone and the donor-to-acceptor charge transfer process in these compounds were confirmed by charge density studies. The β obtained from charge density study are consistent with the HRS findings. All the subject compounds show very promising NLO responses which reflect on the success of the prediction work. In particular, the $\beta_{HRS}$of the compound, 1-methyl-2-((2,4,5,7-tetranitro-9H-fluoren-9-ylidene)methyl)pyrolidine, is 1585±90 $\times 10^{-30}$ esu, which is the largest value in this category reported to date.

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Keywords: charge density study, hyper-Rayleigh scattering, data-mining

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Polytype of illite clays solved by charge flipping

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Polytypism is a common phenomenon in clay minerals. The identification of the polytype of illite clays by powder X-ray diffraction is often depended upon the diagnostic reflections, e.g. pair reflections 20-4 and 204 of $2M_2$ illite separating from 11-5, 02-5 and 023 reflections of $2M_1$ illite, pair of 114 and 11-4 of $2M_1$ differing from -112 and 112 of 1M illite. However, when other phase and multi polytypes present, these diagnostic reflections lose their brilliancy and the work for determining the polytype of clay sample becomes difficult. This study tries to use charge flipping [1] to reconstruct the 3-D map of the electron density for different polytypes of illite clays and from which the relative rotation (n×60°) between two basic 2:1 layers could be observed and thus the polytype solution of illite clays can be made.

The Rietveld refinement is used for phase identification and quantitative evaluation. The result shows 75.4% of $2M_2$, 17.3% of $2M_1$ polytype illite and 7.4% of quartz presenting in sample HW-382 (GOF=2.84%). Le Bail fit [2] is well performed and GOF=1.73%. With the help of charge flipping algorithm [3], the 3-D electron density distributions of different illite polytypes are reconstructed. From the maximum electron densities, the corresponding coordinates of atoms in octahedral (M_1-*trans* site and $M_{2,3}$-*cis* site) are derived. The 60° rotation between adjacent M layers of $2M_2$ polytype illite (figure 1A) and the 2×60° rotation between adjacent M layers of $2M_1$ polytype of illite (figure 1B) can be observed. The distortional parameters τ=109.21° and Δz=0.378Å indicate a little elongation and an out-of-plane tilting presenting along/in T sheet of $2M_2$ illite while τ=111.13° and Δz=0.236Å render the thickening and tilting in T sheet of $2M_1$ illite.

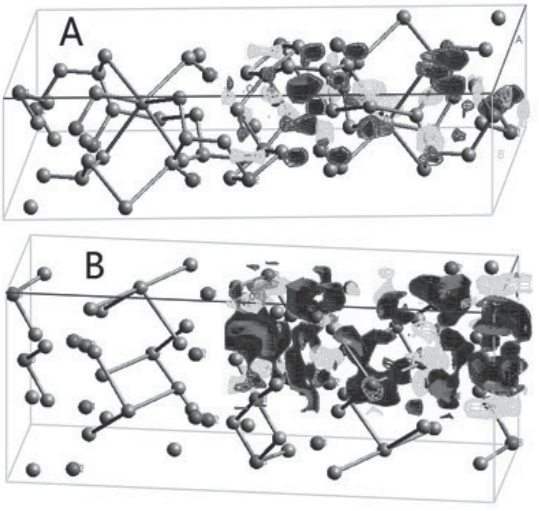

Fig. 1 Crystal structure of illite with 1/8 part overlapped with 3-D electron density distribution. A: $2M_2$ polytype; B: $2M_1$ polytype.

P.MS.41

It is concluded that the charge flipping is a good method to reconstruct the electron density distribution of illite polytype from which the rotation between adjacent M layers can be observed.

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Experimental Electron-Density Analysis without Multipoles

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The extraction of the electron density from the high-resolution X-ray diffraction experiment using the multipole model [1] is a mature technique, which has produced many interesting chemical applications.[2] However, there are known shortcomings in the multipole model regarding the limited flexibility of the employed set of functions to describe the aspherical electron density.[3] We present a new method to model the X-ray diffraction pattern and derive superior molecular geometries as well as electronic properties that go beyond the standard topological analysis of the electron density.

1) *Hirshfeld-atom refinement*.[4] The geometry is refined by using an Hirshfeld-type stockholder partitioning scheme based on ab-initio uantum-mechanical aspherical electron densities. With good data, precise anisotropic displacement parameters can be obtained even for hydrogen atoms.

2) *X-ray constrained wavefunction fitting*.[5] Using the final molecular geometry from 1), a wavefunction is fitted to the experimental data to reproduce the diffraction pattern and simultaneously minimize the molecular energy. In contrast to the multipole model, any basis set can be used.

3) *Electron-density analysis*. The electron density is derived from the constrained wavefunction. Visual inspection and analysis of the residual or static deformation densities serve as a test for the successful reproduction of the experimental crystal density. Subsequently a topological analyses using Bader's Quantum Theory of Atoms in Molecules can be carried out.

4) *Wavefunction analysis*. Several other molecular and electronic descriptors can be calculated from the constrained wavefunction which are not accessible through a multipole description and were thus not obtainable with respect to experimental data before. This includes *energies, electron-localization functions*, *bond orders and bond indices*. We will focus on information about electron-pair localization as derived from the Electron Localizability Indicator (ELI, [6]) and about bond orders as derived from the delocalization index [7] and the Roby bond index [8].

We will discuss the variety of chemical information that can be gleaned from the descriptors in 3) and 4) and contrast this with what is available from only the multipole model.

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Electrostatics of host-guest interactions from charge density analysis of neutral complexes of 18-crown-6

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Electrostatic interactions play a central role in all host-guest interactions. The electrostatic potential (ESP) and, to a lesser extent, the electric field (EF), have been invoked in rationalizing biological processes for several decades. Host-guest chemistry of clathrates and crown ether complexes sits at the foundations of supramolecular chemistry, yet many of these simpler systems have been largely bypassed by today's researchers. The 18-crown-6 bis(guest) centrosymmetric trimer is a common motif formed with a wide variety of small guest molecules, and we have recently measured charge density-quality X-ray diffraction data for many of them. A focus of these studies is the polarization and dipole moment of guest molecules, as this property of the guest is an excellent probe of the electrostatic nature of the hosts.

As an example, charge density analysis for the formamide complex reveals that the magnitude of the EF in the vicinity of the formamide guest molecule is relatively constant (see figure below) and around 16 GV m^{-1}. The vector EF averaged over the formamide nuclei has been applied to an isolated molecule in an *ab initio* calculation to determine the extent of polarization resulting from a field of this magnitude. At the HF/cc-pVTZ level of theory, the molecular dipole moment is 4.50 D in the absence of a field, and 6.14 D with the field applied, an enhancement of 36%. This increase is in line with the estimate of 31% for the hydrogen-bonded crystal of formamide using dipole lattice sums [1]. The theoretical dipole moment in this applied field agrees well with the value of 6.9 ± 0.5 D computed directly from the multipole refinement.

This appears to be the first time that a molecular dipole moment determined from X-ray diffraction data has been rationalised quantitatively on the basis of the electric field it experiences in the crystal. Detailed results of this kind for several complexes of 18-crown-6 will be presented. As it is typically neglected in considerations of host-guest chemistry, the implications of this electrostatic description for a fuller and more detailed understanding of intermolecular interactions in supramolecular chemistry will also be discussed.