

Poster Sessions

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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 β_{HRS} of the compound,

1-methyl-2-((2,4,5,7-tetranitro-9H-fluorene-9-ylidene)methyl)pyrrolidine, is $1585 \pm 90 \times 10^{-30}$ esu, which is the largest value in this category reported to date.

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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 ($n \times 60^\circ$) 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 $2 \times 60^\circ$ rotation between adjacent M layers of $2M_1$ polytype of illite (figure 1B) can be observed. The distortional parameters $\tau=109.21^\circ$ and $\Delta z=0.378 \text{ \AA}$ indicate a little elongation and an out-of-plane tilting presenting along/in T sheet of $2M_2$ illite while $\tau=111.13^\circ$ and $\Delta z=0.236 \text{ \AA}$ render the thickening and tilting in T sheet of $2M_1$ illite.

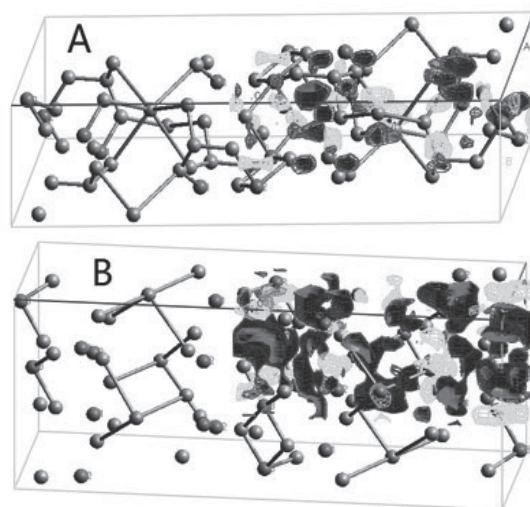


Fig. 1 Crystal structure of illite with 1/8 part overlapped with 3-D electron density distribution. A: $2M_2$ polytype; B: $2M_1$ polytype.