

Data Mining for Terahertz Generation Crystals

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Abstract: We discover, develop, and test new organic nonlinear optical crystals that produce intense pulses of terahertz radiation through a combination of data mining from Cambridge Structural Database and density functional theory calculations. © 2022 The Author(s)

1. Introduction

The discovery and design of advanced organic materials with useful properties is essential to the advancement of many fields, including nonlinear optics, catalysis and electron transport. These unique properties are closely related to the molecular building blocks and structure of the materials [1]. However, it is very time-consuming and costly to identify and develop possible candidates through trial and error. Fortunately, the advancement of computational methods and development of material databases greatly enhance the process of identifying possible candidates for specific uses. Computational methods, such as density functional theory (DFT) calculation, calculates the properties of molecules while material databases can be used to provide required input information for the calculation such as atomic position, molecular bonding and charges of molecules. One potential use of such databases is to identify already existing materials that may be ideal for applications other than their original intended use. The idea that one can easily mine information about known materials for the development of new and extremely useful purposes will rapidly accelerate the discovery of new materials for many applications. This data mining approach also gives rise to new screening methodologies in the rapidly growing field of materials informatics.

Terahertz radiation, with frequencies from 1-10 THz (wavelengths of 300-30 μm), exhibits unique interactions with many materials and thus THz light can be used to analyze and control material properties in ways that differ from other forms of radiation. Many emerging and potentially disruptive applications of THz spectroscopy are taking advantage of these unique interactions, including in bioimaging and security [2], chemical recognition [3], non-destructive chemical monitoring in industry and food processing [4], and wireless communication and high-speed computational devices [5]. Of the various methods available for generating THz light, optical rectification of infrared (IR) light with organic nonlinear optical (NLO) crystals is the most efficient method to produce high-intensity THz fields with extremely broad bandwidths [6]. Organic crystals are efficient in optical rectification due to the fact that the organic molecules have high hyperpolarizability and the crystal packing can be easily modified by modifying the molecular building blocks.

In this report we combine data mining of known organic materials from the Cambridge Structural Database (CSD) with DFT calculation of key molecular properties to identify new candidate organic materials for intense terahertz (THz) generation. We then validate our combined data mining and computational approach to materials discovery by synthesizing and fully characterizing four new THz generating organic materials.

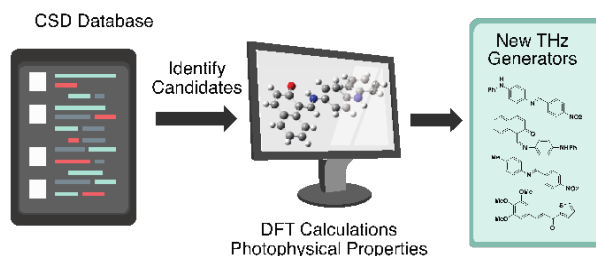


Fig. 1. Data Mining Approach to Material Identification

2. Results

Our data mining effort focused on compounds that contain conjugated π -systems, neutral molecules with light atoms (lighter than Br) and non-centrosymmetric crystal. From a starting pool of over 1 million materials, 15,782 compounds from the CSD were isolated based on our selected criteria. All the resulting compounds were submitted

for DFT hyperpolarizability calculations. A crystal packing order parameter indicates the degree of optimal packing in a molecular crystal for NLO applications. An automated calculation of the order parameter was also performed to quantify molecular alignment of those crystal structures. We selected 10 molecules with high hyperpolarizability and good molecular alignment to be our candidates for THz generation. Out of the candidates, four were synthesized on a large scale and were amenable to large crystal growth, namely PNPA, ZPAN, NMBA and TMOAT. In order to verify that the structures of the grown crystals matched the reported CSD structures, single crystal X-ray diffractometry was used. The structures of all four crystals are consistent with the previously reported structures.

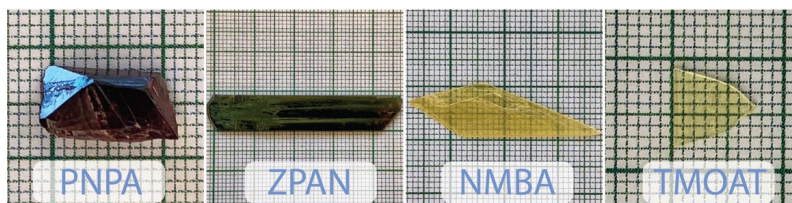


Fig. 2. Large single crystals grown via slow evaporation protocols (square = 1 mm²).

To test the THz generation capability of the four new promising THz generators, we pumped all four crystals with either 1450-nm or 1250-nm pump wavelength based on the crystal colors and compared the spectrums to current state-of-the-art organic THz generators (DAST, OH1 and BNA).

All four new identified crystals also generates THz (Fig. 3). In the red crystal category, we compared THz generation from an PNPA and a ZPAN crystal with industry-standard THz generators DAST and OH-1 by irradiation at 1450 nm pump wavelength under the same conditions. The THz spectrum of PNPA exceeds that of both OH1 and DAST, with a spectral peak at 1 THz. In the yellow crystal category, the THz generation of NMBA is very broadband, and it is comparable to that of BNA.

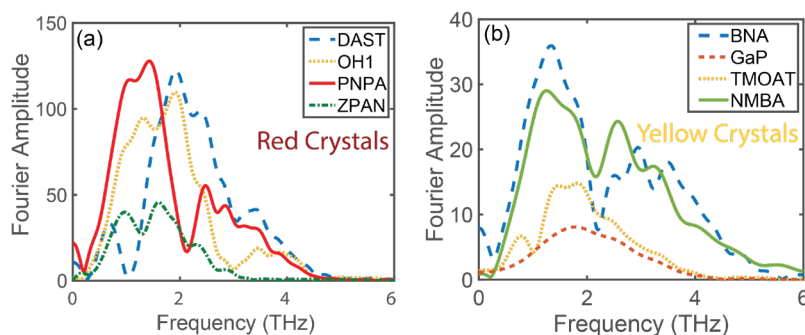


Fig. 3. a) Spectra of red crystals pumped at 1450 nm b) Spectra of yellow crystals and GaP pumped at 1250 nm.

3. Conclusion

Our combination approach of data mining and DFT calculation enables the rapid identification of new organic nonlinear optical material for intense THz generation. This approach is not limited in the THz field, and it is also highly applicable to other fields of material discovery and development.

4. References

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