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A New Screening Methodology for Terahertz Generation Crystals

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***Abstract*—Organic nonlinear optical (NLO) crystals are effective in light frequency conversion through nonlinear optical applications, such as optical rectification and second-harmonic generation, due to low dielectric constants and high molecular hyperpolarizabilities. Yet only a few organic NLO materials have been identified. Combining data mining for structures from the Cambridge Structural Database and density functional theory calculations, we discover new organic nonlinear optical crystals that generate intense terahertz (THz) radiation. To confirm our combination approach, we recrystallized and tested the newly discovered organic nonlinear materials. The results of THz experiments showed the THz generation capabilities exceed state-to-art THz generation crystals (DAST, OH-1 and BNA).**

I. Introduction

Designing solid organic materials with useful properties is vital in many fields, such properties are closely related to the molecular building blocks and the structure of materials[1]. Rather than time-consuming and costly trial and error, one powerful alternative method to identify possible candidates for specific uses is the use of computational method and material databases. Computational methods, such as density functional theory (DFT), can calculate properties of materials while material databases provide required molecular or structure input for the calculations. 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.

One noble field of material developments is nonlinear optical (NLO) crystals, which are one of the main components in optical communication systems and optical sensing, due to their unique abilities in light frequency conversion through nonlinear processes. In recent years, many researchers have been able to use NLO crystals to generate intense light frequencies that were not widely accessible due to technical difficulty in the past, for example, generating intense Terahertz (THz) radiation with extremely broad bandwidths[1] through optical rectification of infrared (IR) light. THz light is of particularly interest as its frequency range is very similar to the vibrational frequencies of collective atomic motions in a host of materials, thus THz light can efficiently interact with these collective motions. Due to this advantage, THz can be used to analyze and control material properties in unique 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, chemical recognition, non-destructive chemical monitoring in industry and food processing, and wireless communication and high-speed computational devices[2].

To maximize THz generation capability, a NLO crystal must be packed into a noncentrosymmetric space group and its molecular building blocks must have high hyperpolarizability. One can easily estimate the value of hyperpolarizability through many widely accessible DFT programs. However, predicting and achieving successful crystal packing for molecules has proven to be exceedingly difficult. Therefore, while the need for THz generating NLO materials is growing, only a few such NLO crystals have been developed, such as DAST, OH1 and DSTMS.

To overcome this difficulty, 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 THz generation. We further validate our combined data mining and computation approach to materials discovery by synthesizing and fully characterizing the crystallographic structures and the THz generation capability of four new THz generating organic materials via single-crystal X-rays diffractometry and electro-optical sampling.

II. Results

In our early round of data mining search of CSD, we were able to identify a headful of noncentrosymmetric crystals that are capable in THz generation[3]. Since then, we expanded our dataset to also include chiral neutral molecules. From a starting pool of over 1.1 million materials, 65,950 compounds from the CSD were isolated based on our selected criteria. To evaluate the THz generation capabilities of the extracted structures, the molecular building blocks were submitted for DFT hyperpolarizability (β) calculation and crystal packing order parameter (OP) calculation (Table 1). Order parameter accounts for the molecular alignment in the crystalline state, which is directly related to THz generation capability of materials (The value is between 0 to 1 – a value of 1 represents ideal head-to-tail alignment). Out of the candidates, four crystals with high β and various OP values were synthesized on a large scale and were amenable to large crystal growth, namely PNPA, ZPAN, NMBA and TMOAT.

ID	β (esu)	OP	ID	β (esu)	OP
PNPA	3.16×10^{-28}	1	NMBA	8.19×10^{-29}	0.84
ZPAN	9.52×10^{-29}	0.55	TMOAT	5.08×10^{-29}	0.39
OH1	1.95×10^{-28}	0.83	DAST	8.96×10^{-29}	0.68

Table 1. Calculated β and OP values for mined structures and well-known THz generators (OH1 and DAST).

The structures of all four crystals were verified to be consistent with the previously reported structures in CSD through single crystal X-ray diffractometry.

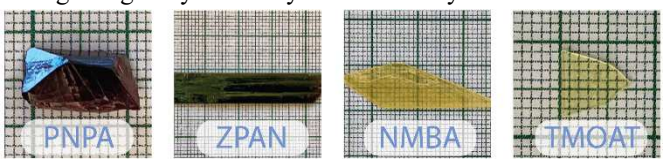

Fig. 2. Large single crystals grown via slow evaporation protocols (square = 1 mm2).

To test the THz generation capability of the four new promising THz generators, we pumped the crystals with either 1450-nm or 1250-nm pump wavelength based on the crystal colors and compared the spectra to current state-of-the-art organic THz generators (DAST, OH-1 and BNA). The crystals were pumped with different wavelengths of light based on their colors as yellow organic crystals often exhibit higher efficiency at shorter wavelengths than the red organic crystals.

All four newly identified crystals exhibit efficient THz generation capability, especially for red PNPA and yellow NMBA crystals. When irradiating with 1450-nm pump wavelength under the same conditions, The THz spectrum of a 850 μm thick PNPA exceeds that of industry-standard THz generators DAST (470 μm) and OH-1 (300 μm). The THz spectrum of PNPA has a spectral peak at 1 THz. (Fig. 3a). This result is consistent with the hyperpolarizability and order parameter calculations, which PNPA has the largest β and OP values.

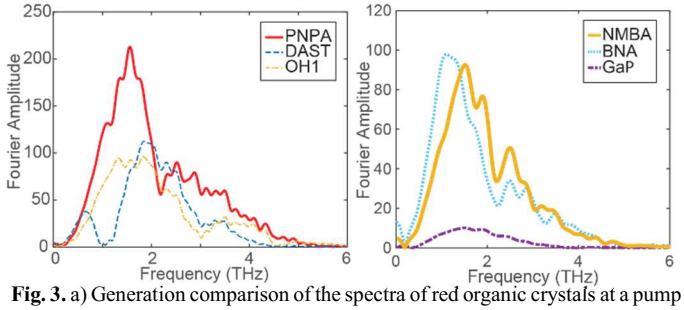

Fig. 3. a) Generation comparison of the spectra of red organic crystals at a pump wavelength of 1450 nm. b) Generation comparison of the spectra of yellow organic crystals pumped at 1250 nm (and inorganic GaP).

In the yellow crystal category, a 370 μm thick NMBA were compared with a well-known yellow BNA crystal (400 μm thick) and red inorganic crystal GaP (300 μm) by irradiation at 1250 nm pump wavelength under the same conditions. The THz generation of NMBA is very broadband, and its spectroscopic shape and amplitude of the Fourier transform are comparable to that of BNA (Fig. 3b).

Because of this initial success in predicting THz capability through our hyperpolarizability and order parameter calculations, we decided to incorporate a more complete model to further assess the THz generation capability of structures based on both molecular alignment and hyperpolarizability. We calculated the polarization of the crystals based on second order susceptibility tensor using the two equations below[4]:

$$\left[d_{IJK}(0\omega;\omega,\omega)\right] = \left[Nf\sum_{\substack{s=1\\i,j,k}}^{n} cos\big(I,i(s)\big)\,cos\big(J,j(s)\big)\,cos\big(K,k(s)\big)\,\beta_{ijk}(s)\right] \quad (1)$$

$$\begin{bmatrix}P_X\\P_Y\\P_Z\end{bmatrix} = 2\epsilon_0\left[d_{IJK}(0\omega;\omega,\omega)\right]\begin{bmatrix}E_x^2\\E_y^2\\E_z^2\\2E_yE_z\\2E_xE_z\\2E_xE_y\end{bmatrix} \quad (2)$$

In eqn. 1, N is the crystal density and f is the Lorentz local-field factor. The summation of the cosine product terms converts from the molecular reference frame (i, j, k) to the crystallographic reference frame (I, J, K) over all the molecules (n) in a unit cell. β_{ijk} is the molecular hyperpolarizability vector.

In eqn. 2, the three P terms represent the polarizations in THE three crystallographic directions. d_{IJK} term is the susceptibility tensor, and the E terms account for different polarization of the input pump light.

Calculating induced crystal polarization is very valuable because the THz radiation amplitude is directly correlated to the 2nd time derivative of the polarization of the crystal[5]. This can be used to account for THz capability of crystal more directly and comprehensively.

Table 1 shows the maximum polarization values for our previously test THz generation crystals. The relative order of the calculated polarization values for the red crystals are consistent to the relative THz generation performance shown in fig. 2a. For the yellow crystal side, the relative order is also consistent except for the BNA crystal. This indicates the calculated polarization values can predict for THz generation capability.

Red Crystal	P_{max}	Yellow Crystal	P_{max}	New Crystal (CSD ID)	P_{max}
DAST	37.39	BNA	4.36	YISCIM	114.39
OH1	17.93	NMBA	15.03	BIQSOJ	81.60
PNPA	71.21	TMOAT	8.03	QIRCID	59.24
ZPAN	13.16			WIDXAK	37.42

Table 2. Polarization values for state-to-art crystals, newly tested crystals and potential candidates.

III. Summary

These results show the great potential for our combination approach of data mining and DFT calculation, which also confirm that our combined approach can indeed provide a productive and powerful method for identifying new organic materials for THz generation and even predicting relative THz generation capabilities. This combined approach is not limited to only the field of THz, but it is also highly applicable in any fields of materials discovery and development.

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