

First-Principles Screening of Metal-Organic Frameworks for Entangled Photon Pair Generation

Sanoj Raj^{1,4}, Simón Paiva², Rubén A. Fritz², Felipe Herrera^{2,3}
and Yamil J. Colón¹

¹ Department of Chemical and Biomolecular Engineering, University of Notre Dame, IN 46556, USA

² Department of Physics, Universidad de Santiago de Chile, Av Victor Jara 3493, Santiago, Chile

³ Millennium Institute for Research in Optics, Concepción, Chile

⁴ Current address: Department of Chemistry, Bowdoin College, ME 04011, USA

E-mail: ycolon.nd.edu; felipe.herrera.u@usach.cl

Abstract. The transmission of strong laser light in nonlinear optical materials can generate output photons sources that carry quantum entanglement in multiple degrees of freedom, making this process a fundamentally important tool in optical quantum technology. However, the availability of efficient optical crystals for entangled light generation is severely limited in terms of diversity, thus reducing the prospects for the implementation of next-generation protocols in quantum sensing, communication and computing. To overcome this, we developed and implemented a multi-scale first-principles modeling technique for the computational discovery of novel nonlinear optical devices based on metal-organic framework (MOF) materials that can efficiently generate entangled light via spontaneous parametric down-conversion(SPDC). Using collinear degenerate type-I SPDC as a case study, we computationally screen a database of 114,373 synthesized MOF materials to establish correlations between the structure and chemical composition of MOFs with the brightness and coherence properties of entangled photon pairs. We identify a subset of 49 non-centrosymmetric mono-ligand MOF crystals with high chemical and optical stability that produce entangled photon pairs with intrinsic $G^{(2)}$ correlation times $\tau_c \sim 10 - 30$ fs and pair generation rates in the range $10^4 - 10^8 \text{ s}^{-1}\text{mW}^{-1}\text{mm}^{-1}$ at 1064 nm. Conditions for optimal type-I phase matching are given for each MOF and relationships between pair brightness, crystal band gap and optical birefringence are discussed. Correlations between the optical properties of crystals and their constituent molecular ligands are also given. Our work paves the way for the computational design of MOF-based devices for optical quantum technology.

Keywords: Metal-Organic Frameworks, Spontaneous Parametric Down Conversion, Entangled Photons, Energy-Time Entanglement

1. Introduction

Entangled photon pair generation is a fundamental technique in quantum optics and quantum information science [1, 2, 3, 4, 5]. Correlations between entangled photons can be exploited in various applications, such as quantum teleportation [2], quantum computing, quantum cryptography [6, 7, 8, 9], and quantum imaging [10, 11, 12]. Spontaneous parametric down-conversion (SPDC) is a widely used method for generating entangled photon pairs. SPDC occurs when a high intensity laser pump (p) interacts with a nonlinear crystal and, as a result of the interaction, pairs of low energy photons are spontaneously generated. The pair components are denoted signal(s) and idler(i) [13]. The output photons must obey conservation relationship in terms of their angular frequencies and wave vectors ($\omega_p = \omega_s + \omega_i$, $\vec{k}_p = \vec{k}_s + \vec{k}_i$) [13, 14]. The SPDC process can be divided into types, degeneracy and direction. In type-I SPDC, the generated photons have the same polarization while in type-II, the output photons have orthogonal polarization. The system is collinear if the photons have the same propagation direction as the pump and non-collinear if they propagate in different directions. Figure 1 shows a schematic diagram of the SPDC process, highlighting energy and momentum conservation. SPDC ($2\omega \rightarrow \omega$) and second harmonic generation ($\omega \rightarrow 2\omega$) are conjugate processes in nonlinear optics which differ on how they are experimentally implemented [13]. For a material to be SPDC efficient and have high performance over a wide range of bandwidths, it should have high nonlinear susceptibility, suitable phase matching, optical transparency (high band gap), thermal stability and be suitable for practical operation (low cost, availability, ease of use).

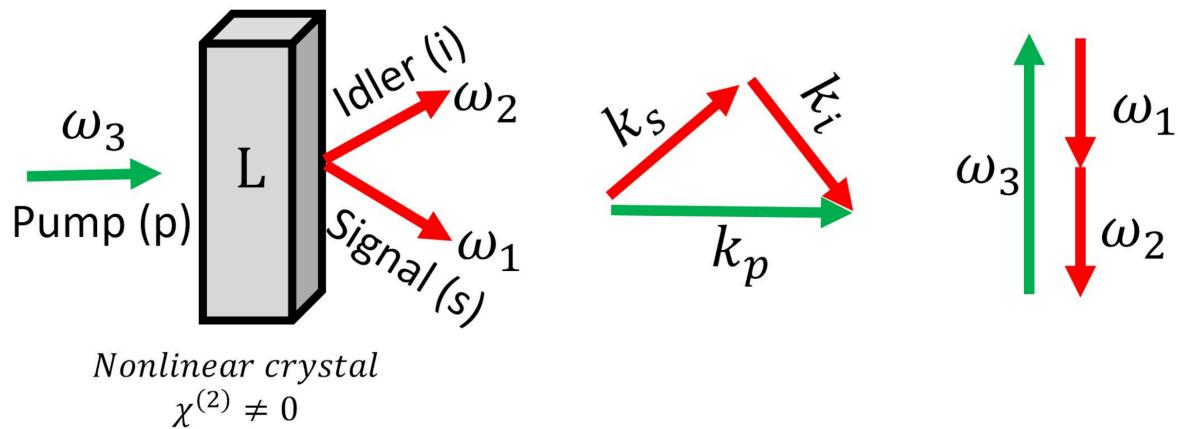


Figure 1. Schematic of SPDC process with momentum and energy conservation. One photon energy $\hbar\omega_3$ splits into two twin photons at energies $\hbar\omega_1$ and $\hbar\omega_2$.

The ability of nonlinear optical materials to be phase matchable depends on whether they belong to non-cubic crystal classes or not. Birefringence phase matching (BPM) depends on the difference of refractive indices at specific wavelengths and is only possible for anisotropic crystal systems (non-cubic). The non-cubic crystal class is divided into

groups: biaxial and uniaxial [13]. Triclinic, monoclinic and orthorhombic crystal systems are biaxial, and trigonal, tetragonal and hexagonal are uniaxial. In terms of refractive indices, uniaxial crystals have $n_X = n_Y \neq n_Z$ and biaxial crystals have $n_X \neq n_Y \neq n_Z$. For non-linear optical (NLO) applications it is important that the crystal is non-centrosymmetric (NCS) as they have non-zero second order non-linear susceptibility tensor ($\chi^{(2)}$) which defines the efficiency of the process [13]. Uniaxial and biaxial crystals can be further divided into crystal class and the list of all the crystal classes which are NCS is known.

The effective non-linearity, d_{eff} , obtained by contracting the $\chi^{(2)}$ with the field polarization of suitable birefringence phase matching condition, is an intrinsic property of materials and plays a crucial role in developing modern optical devices as well as entangled photon sources with high brightness (number of entangled photons) [15]. The brightness of the signal scales as the square of d_{eff} , linearly with the pump power, and linearly with propagation length (L) [16, 17] when crystals have a random orientation (powder) and scales as L^2 for a single crystals. The effective non-linearity is affected by several material factors such as the electronic structure, chemical composition, optical properties, microstructure, temperature and pressure [18, 9, 19, 20, 21, 22, 23, 24, 25, 26].

BBO, LiNbO₃, KDP, and other leading materials, have been experimentally realized for nonlinear optical process but have relative disadvantages such as absence of electron delocalization, and the inability to adjust their structures [27]. Organic materials have been proposed to resolve these deficiencies but they lack good mechanical strength and thermal stability. Metal-organic frameworks (MOFs) are hybrid materials consisting of metal ions or clusters coordinated to organic ligands to form 1D, 2D or 3D structures, which have shown promise for nonlinear optical process as they can combine the benefits of inorganic and organic compounds [28, 29]. MOFs offer interesting possibilities in terms of synthesis of new structures with high flexibility and tunability, which allows for the optimization of their optical properties. The organic linkers in MOFs can be tuned to achieve a large nonlinear optical response and the metal centers can provide high degree of anharmonicity, which can significantly enhance the nonlinear optical response [18, 27]. MOFs offer high surface area, and are stable under various conditions and can be synthesized with a high degree of control over their size, shape and functionality. Several MOF structures have been experimentally synthesized and some of them have already shown potential to be used in nonlinear optics [30, 31, 32, 33, 34, 35, 36, 37]. A recent publication reports the experimental demonstration of three-wave and four-wave mixing processes using millimeter-scale MOF single crystal with well-defined phase matching properties [38]. The competitive optical nonlinearities of several polycrystalline MOF samples have stimulated the need to develop a robust computational methodology to screen the MOF databases to understand the structure-property relationship to identify and design potential MOF crystals that are promising.

In previous work, we developed a multi-scale methodology to compute entangled photon pair properties for uniaxial MOF crystals [15]. We have also shown that the types of ligand and their arrangement can significantly affect the entangled photon

pair properties [39]. In this work, we extend our methodology to take into account the calculation of d_{eff} for biaxial crystals with appropriate phase matching condition, photon correlation ($G^{(2)}$) function and counting rate of entangled photon pairs for the collinear type-I SPDC. We have carried out high-throughput screening of MOFs with zinc as a metal and one-type of ligand to understand how different structures affect the properties of the entangled photon source. Based on our results, we provide design rules which can be used to develop new materials which are highly SPDC efficient.

2. Methods

MOF selection criteria and computational details: Figure 2 shows the flowchart of the MOF filter. After applying the selection criteria, we obtained a database of mono-ligand MOFs with Zn as a metal. All the MOFs in our database are experimentally synthesized and they come from the Cambridge Crystallographic Data Center (CCDC).

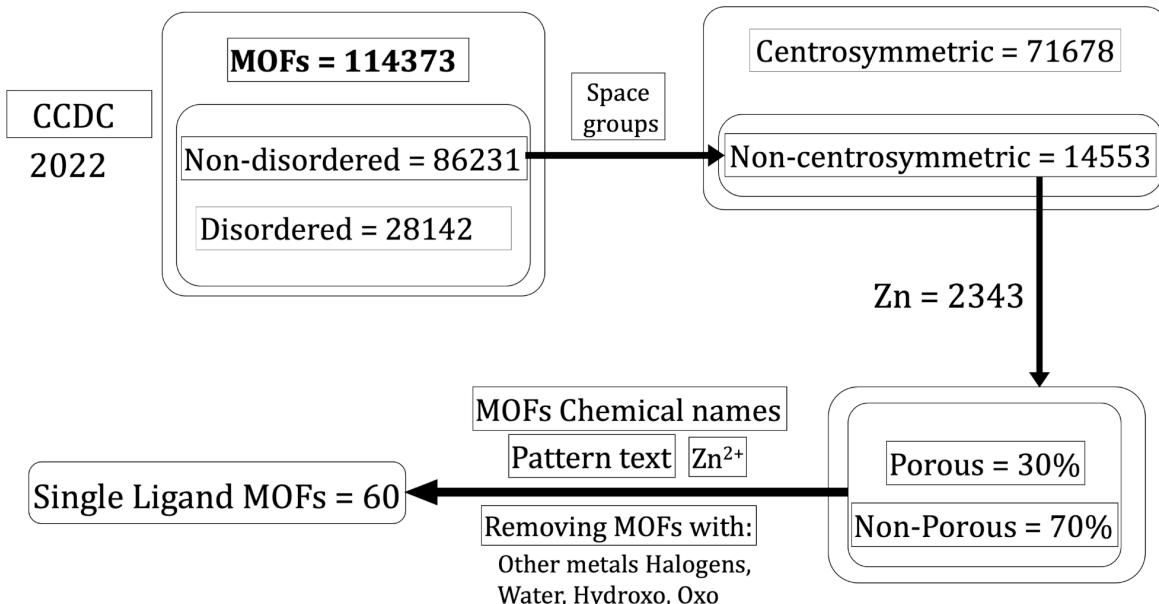


Figure 2. Flowchart of the MOF selection filter.

We used VESTA [40] to manipulate and clean the original cif file, which was obtained from the CCDC. The software suite ISOTROPY [41] was used to identify the space group of MOF crystals. All the crystal structures were optimized using POB-DZVPP basis set with shrink points 3 3 and TOLINTEG 12 12 12 12 12 18. We also added DFT-D version 4 for the dispersion correction. We used solid-state DFT within the Coupled Perturbed Hartree-Fock/Kohn-Sham method (CPHF/KS) [42, 43, 44] with a PBE functional to compute the dynamical dielectric tensor $\epsilon_{ij}(\omega)$ and the dynamical second-order susceptibility tensor $\chi_{ijk}^{(2)}(\omega)$ of the optimized structures. We have used CRYSTAL17 [45] package to carry out all the DFT calculations. We benchmarked these methods in previous work [15]. We also used available KDP and BBO data to

compare as an additional benchmark. The TOLINTEG and SHRINK points sampling were also done to check the energy convergence. Also, the same DFT method was used in previous works for optical measurement of MIRO-101 single crystal [37] and to study the affect of arrangement of ligands and temperature on entangled photon pair properties [39].

Effective nonlinearity estimation: The estimation of the effective non-linearity (d_{eff}) of a given crystal is carried out in the orthogonal coordinate system X Y Z in which the dielectric tensor ϵ_{ij} is diagonal. A crystal is considered uniaxial (with optic axis Z) if $\epsilon_{XX} = \epsilon_{YY} \neq \epsilon_{ZZ}$, and biaxial (with the optic axis in the plane XZ) if $\epsilon_{XX} \neq \epsilon_{YY} \neq \epsilon_{ZZ}$, and one of two relations being fulfilled: $n_X > n_Y > n_Z$, or $n_Z > n_Y > n_X$, where $n_X^2 = \epsilon_{XX}$, $n_Y^2 = \epsilon_{YY}$, $n_Z^2 = \epsilon_{ZZ}$ are the principal values of the refractive indices. For some biaxial crystals (crystal class 1, 2 and m), the dielectric matrix is not diagonalizable [13]. In those cases, the trace of dielectric matrix gives the refractive indices.

Uniaxial and biaxial crystals can be further divided into positive or negative as discussed in the Supporting Information (SI) section 1. For biaxial crystals, it is possible that the principal values of refractive indices in the crystallographic frame (a, b, c) are different than the crystallophysical frame (X, Y, Z). Crystallophysical, optical and dielectric frame represent the same concept. Among many widely used crystals such as KTP, KNbO₃, LBO [46], BiBO [47] and α -HIO₃, the coordinate system X, Y, Z and a, b, c can coincide or misconcide. In KTP, the coordinate systems coincide and we can designate the coincidence as $X, Y, Z \rightarrow a, b, c$ whereas for LBO, the assignment $X, Y, Z \rightarrow a, c, b$ is commonly used [46]. It is important to do the necessary transformation of the crystallographic frame (a, b, c) to satisfy the biaxial condition [46, 48] ($n_Z > n_Y > n_X$) and then calculate the d_{eff} for different polarization configurations after doing the necessary transformation of the $\chi^{(2)}$ tensor. d_{eff} was estimated using a specific configuration by contracting the full second-order polarizability tensor at the phase matching angles for different crystal structures. Figure 3 shows the flowchart for calculating d_{eff} of any given crystal. Detailed description for calculating birefringence, phase matching angles, d_{eff} , $G^{(2)}$, and number of entangled photons can be found in SI section 1. Data and code are available on GitHub ([Codes and data](#)) for reproducibility.

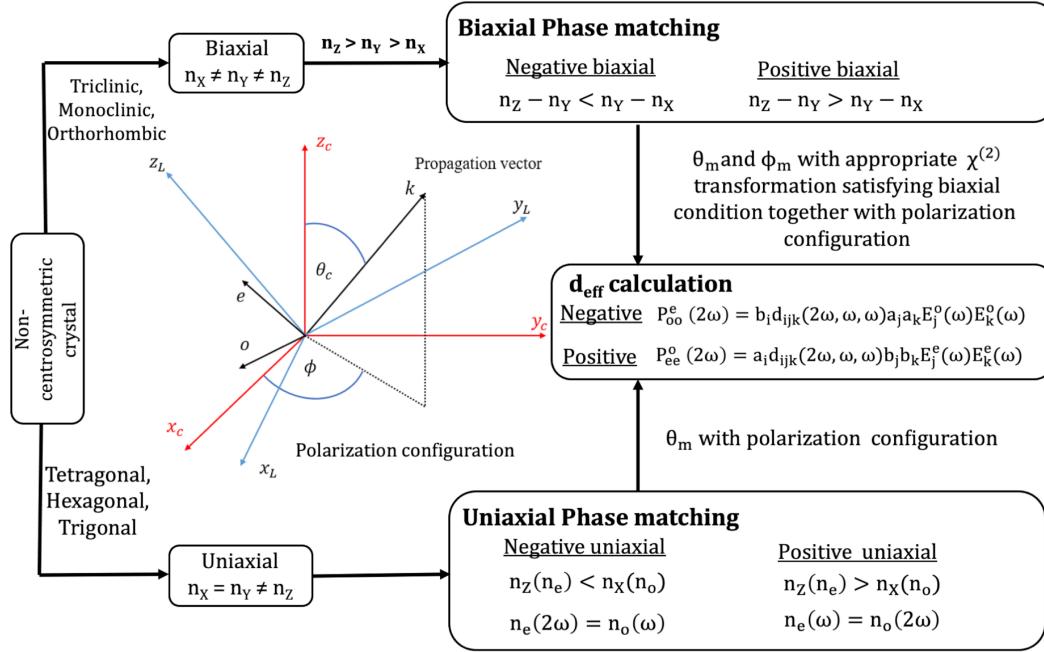


Figure 3. Flowchart for calculating d_{eff} of any given crystal. n_X , n_Y and n_Z are the refractive indices. n_o and n_e are the ordinary and extraordinary refractive indices. The crystal optic axis Z_c sets a polar angle θ_c and azimuthal angle ϕ with respect to the propagation direction k . d_{eff} is obtained by contracting the $\chi^{(2)}$ tensor with appropriate polarization configuration.

An important feature for applications of entangled photon pairs is the correlation time between the two generated photons (τ_c). This parameter can be defined as the full width at half maximum (FWHM) of the $G^{(2)}$ correlation function. This correlation function not only depends on the crystal properties, but also on the properties of the experimental set-up such as the bandwidth of the detector [49]. For type-I SPDC the $G^{(2)}$ function can be written as

$$G^{(2)}(\tau) \propto \left| \int_{-\infty}^{\infty} d\nu \operatorname{sinc}\left(\frac{\kappa\nu^2 L}{4}\right) e^{-\left(\frac{\nu^2}{\sigma^2}\right)} e^{-i\nu\tau} \right|^2 \quad (1)$$

where ν correspond to a small detuning frequency from the perfect phase matching, κ is the group velocity dispersion (GVD), L is the crystal length and σ is the bandwidth of the detector.

We also assume a Gaussian model for the transverse field profile of the pump and the two generated photons (signal and idler), collecting the down-converted light into single-mode fibers such that the transverse width of the two generated photons is the same $\sigma_1 = \sigma_2$. The single-mode counting rate for photon pairs generated by type-I SPDC is given by [50]

$$R = \frac{|E_p^0|^2 (d_{\text{eff}})^2 L^2}{2\pi c^2} \frac{n_{g1} n_{g2}}{n_1 n_2} \left| \frac{\sigma_p^2}{\sigma_1^2 + 2\sigma_p^2} \right|^2 \int d\omega_1 \omega_1 (\omega_p - \omega_1) \operatorname{sinc}^2 \left(\frac{\Delta k L}{2} \right) \quad (2)$$

where σ_p and σ_1 are the transverse width of the Gaussian profiles associated with the pump and signal or idler photon respectively. n_1 and n_2 are the signal and idler refractive indices, n_{g1} and n_{g2} correspond to the group indices of the signal and idler frequency. c is the velocity of the light, $|E_p^0| = \frac{|D_p^0|}{\epsilon_0 n^2}$ is proportional to the monochromatic pump beam peak magnitude $|D_p^0|$, and $P = c|D_p^0|^2 \pi \sigma_p^2 / n^3 \epsilon_0$ is the amount of power delivered by a Gaussian pump beam. The phase mismatch Δk is given by

$$\Delta k \approx \kappa (\omega_1 - \omega_p)^2, \quad (3)$$

where ω_1 correspond to the frequency of the signal and idler photon and ω_p is the fixed pump frequency.

We have used the pump wavelength of 532 nm for our study and MOFs whose band gap is greater than 2.28 eV. After applying the selection criteria on the band gap, we found 49 MOFs that are suitable for this study.

3. Results and discussions

Birefringence ($\Delta n = n_x - n_z$) plays a crucial role in achieving phase-matching conditions for nonlinear materials. The variations in Δn_{1064nm} for all the crystals used in our study are depicted in Fig. 4A. The MOF crystal AQOROP has the highest Δn and ONOCOL01 has the smallest value. Details about crystal class, band gap and birefringence are shown in SI section 2.

Figure 4B illustrates the relationship between Δn and the band gap for different crystals. We find that Δn decreases with increased band gap. Furthermore, Fig. 4C displays the correlation between the HOMO-LUMO gap of the ligand monomers and the band gap the crystals that contain these ligands. A strong correlation is evident, indicating that HOMO-LUMO gap influences the band gap of the crystal, including a red shift that results from interactions within the crystal. This observation serves as a valuable design criterion for crystals and provides the ability to control the band gap. The ability to control the band gap is very important, particularly in getting transparent crystals. Moreover, Δn holds a key role in achieving phase matching over a wider bandwidth. These features are critical for the advancement of efficient nonlinear optical materials. The careful selection of ligands emerges as a powerful tool to fine-tune these optical properties for desired specifications.

The observations discussed above can be explained by considering the polarizability (α). Polarizability refers to the ease with which the electron cloud of a material can be distorted by an external electric field and is directly linked to the refractive index. A material with higher polarizability, indicating a greater ability for charge separation, will have a higher refractive index and higher Δn [51]. Charge separation and delocalization of electrons are closely related to each other. Highly delocalized electrons lead to higher polarizability which affects the refractive index and Δn . Furthermore, electron delocalization affects the HOMO-LUMO gap for ligand molecules and the crystal band

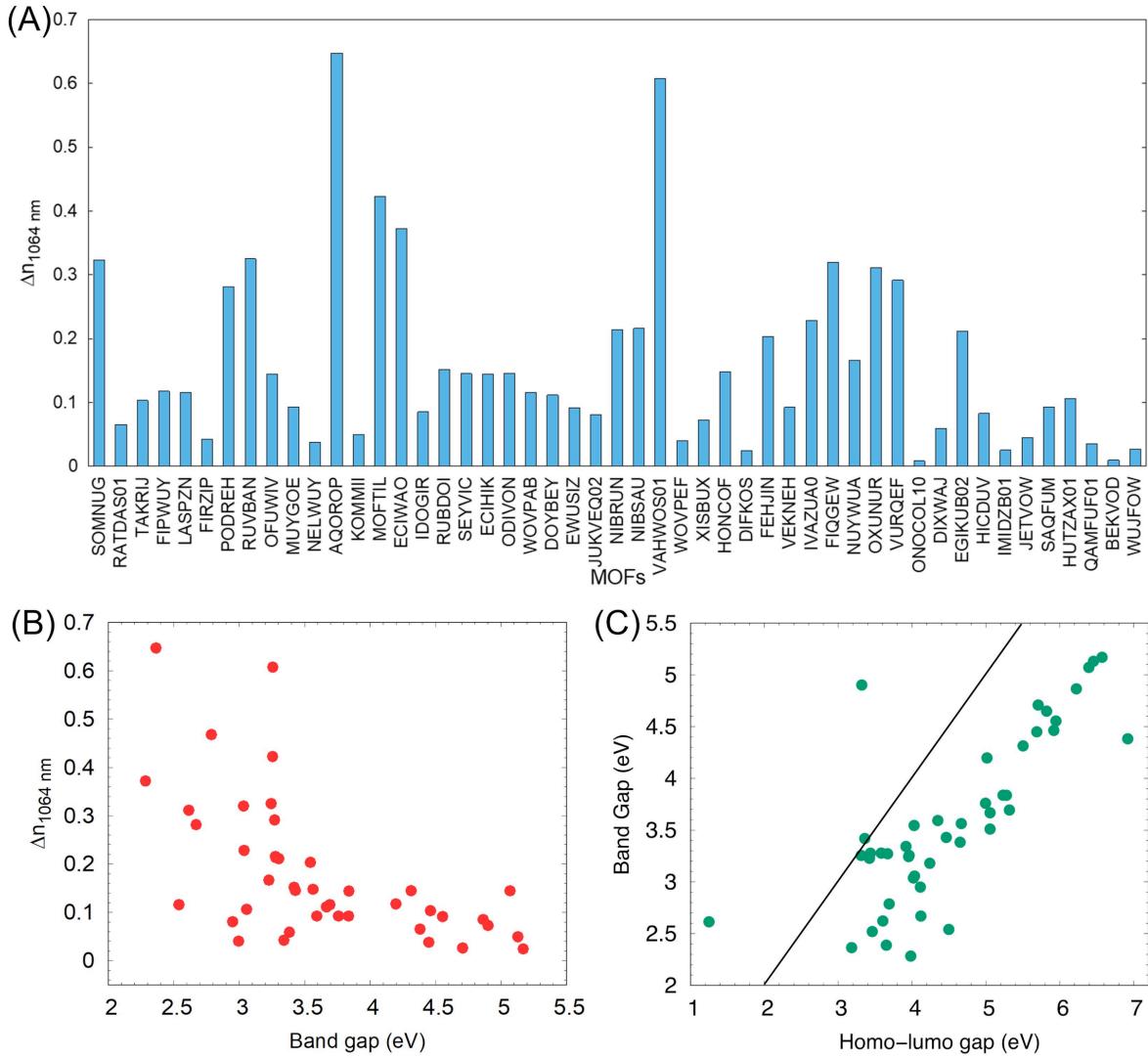


Figure 4. (A) Birefringence Δn for different MOF crystals. (B) Δn as a function of band gap for different MOF crystal. (C) Correlation plot between the homo-lumo gap of the ligands and band gap the crystal which has this ligands. The black line represents the perfect correlation between the band gap and HOMO-LUMO gap.

gap. Higher delocalization of electrons, gives smaller band gaps [52]. Therefore, the energy gap and birefringence are inversely related to each other.

Birefringence and phase-matching are related with each other. An increase in birefringence increases the phase-matching wavelength range which can significantly affect the nonlinear efficiency. It should be noted that if birefringence is too large, serious walk-off effect can occur and nonlinear efficiency can significantly decrease even if the nonlinear coefficients are higher [53, 14]. If the birefringence is too small, phase-matching will not occur. We have calculated the phase-matching angles of all the crystals depending on whether a crystal is uniaxial or biaxial at 1064 nm (see Method section). We benchmarked our method by reproducing phase-matching angles calculations for KTP [54] and BiBO [47, 55] as shown in SI section 3.

For NLO materials to be technologically useful, it is not enough for a material to be highly efficient at a given wavelength but also should be phase matchable. The phase matching angle together with the $\chi^{(2)}$ tensor determine the d_{eff} of the crystal. Figure 5A shows the overlay of possible phase matching angles, shown with black lines, with the 2D map of d_{eff} for all the θ and ϕ for a WOVPA crystal belonging to crystal class 222. It is important to note that although some combination of θ and ϕ can give high d_{eff} , those angles may not be accessible due to phase-matching conditions. Figure 5B shows the phase matching angles (θ_m and ϕ_m) of biaxial crystals belonging to crystal class 222. We observe that although the crystals belong to the same crystal class, they have very different phase-matching angular profiles.

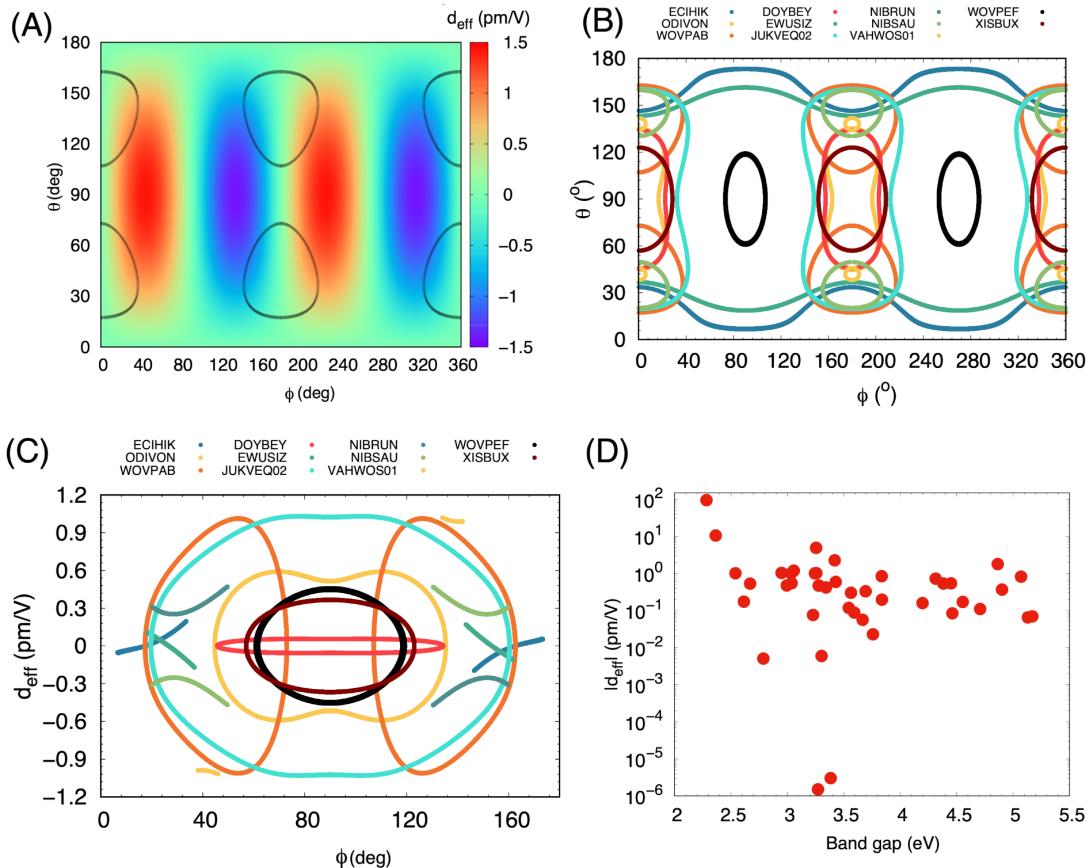


Figure 5. (A) 2d map of d_{eff} as function of θ , ϕ of WOVPA MOF crystal belonging to 222 crystal class. Black lines shows all the possible phase matching angles (θ_m and ϕ_m). (B) Phase matching angles (θ_m and ϕ_m) of biaxial crystals belonging to crystal class 222. (C) d_{eff} of crystals belonging to crystal class 222 as function of phase matching angle, θ_m . ϕ_m is not shown for clarity. (D) d_{eff} as function of band gap for different crystals. Crystals whose d_{eff} values are closer to 10^{-6} pm/V belong to the 422 crystal class.

The effective non-linearity is an intrinsic property of a materials and plays a crucial role in developing modern optical devices as well as entangled photon sources with high brightness (number of entangled photons). The source brightness scales with d_{eff}^2 , and

d_{eff} is used to parameterize the effective Hamiltonian for the SPDC process. In order to calculate d_{eff} at 1064 nm for different crystals, we have divided MOFs into uniaxial and biaxial classes. We have used the phase matching condition to find phase matching angles, θ_m for uniaxial, and θ_m and ϕ_m for biaxial at 1064 nm, and used the appropriate polarization configuration to find the d_{eff} (see Method Section and SI Section 2 for transformation between crystallophysical and crystallographic frame to satisfy biaxial condition). The calculated $\chi^{(2)}$ for all the MOFs used in our study are given in SI Section 4. Figure 5C shows d_{eff} as function of θ (ϕ_m is not shown for clarity) for MOF crystals belonging to crystal class 222. The sign of d_{eff} is unimportant and it is the profile of d_{eff}^2 that dictates the conversion efficiency along a given phase matching direction. Phase matching angles (θ_m) of all the uniaxial crystals are shown in SI Section 2 and phase matching angles (θ_m and ϕ_m) of all the biaxial crystals used in our study are shown in the SI Section 3.

Figure 5D shows the absolute maximum value of d_{eff} of all the crystal as a function of their band gaps. We observe that d_{eff} decreases with increasing band gap. This is because materials with smaller band gaps enable greater degree of overlap between the wavefunctions of electrons and holes and leads to a higher probability on nonlinear optical interactions which can significantly affect the efficiency of the non-linear process. Materials with smaller band gaps lead to higher nonlinearities as compared to higher band gap because their electronic structures enable a greater degree of optical mixing and frequency conversion. We also observe that MOF crystals belonging to crystal class 422 (uniaxial crystal) have $d_{\text{eff}} = 0 \text{ pm/V}$ (see Fig. 5D) although it has small $\chi^{(2)}$ as shown in Fig. S2. This agrees well with the literature as crystals belonging to the 422 crystal class will have vanishing d_{eff} if Kleinman's symmetry is valid [56, 57].

Entangled photon pair properties: The $G^{(2)}(t_1 - t_2)$ intensity correlation function gives the probability of detecting two-photon pairs at different time t_1 and t_2 (see Method section for more details). Figure 6A shows the schematic of coincidence setup for measuring the two-time correlation function $G^{(2)}(\tau \equiv t_1 - t_2)$. Figure 6B shows $G^{(2)}(\tau)$ for some of the MOFs used in this study (see SI Section 4 all the MOFs $G^{(2)}$). The FWHM of $G^{(2)}(\tau)$ gives the pair correlation time (τ_c). Figure 6C shows τ_c as function of band gap for all the crystals. We observe that τ_c decreases with increasing band gap. This is due to higher and smaller degrees of overlap between the wavefunctions of electrons and holes for smaller and larger band gaps. The degree of correlation between the generated photons is relevant in applications such as quantum computing, quantum key distribution, quantum teleportation, and quantum cryptography [6, 7, 9, 2]. We find that AQOROP ($\sim 27.55 \text{ fs}$), ECIWAO ($\sim 24.87 \text{ fs}$) and MOFTIL ($\sim 25.76 \text{ fs}$) have the largest autocorrelation times.

The number of entangled photon pairs generated in SPDC is an important parameter for entanglement-based applications [49]. Figure 6D shows the number of entangled photon pairs generated by all the crystals as function of their d_{eff}^2 . We found that AQOROP ($\sim 7 \times 10^7 \text{ s}^{-1} \text{ mW}^{-1} \text{ mm}^{-1}$), ECIWAO ($\sim 6.6 \times 10^9 \text{ s}^{-1} \text{ mW}^{-1} \text{ mm}^{-1}$) and MOFTIL ($\sim 1.6 \times 10^7 \text{ s}^{-1} \text{ mW}^{-1} \text{ mm}^{-1}$) have the largest photon conversion rates.

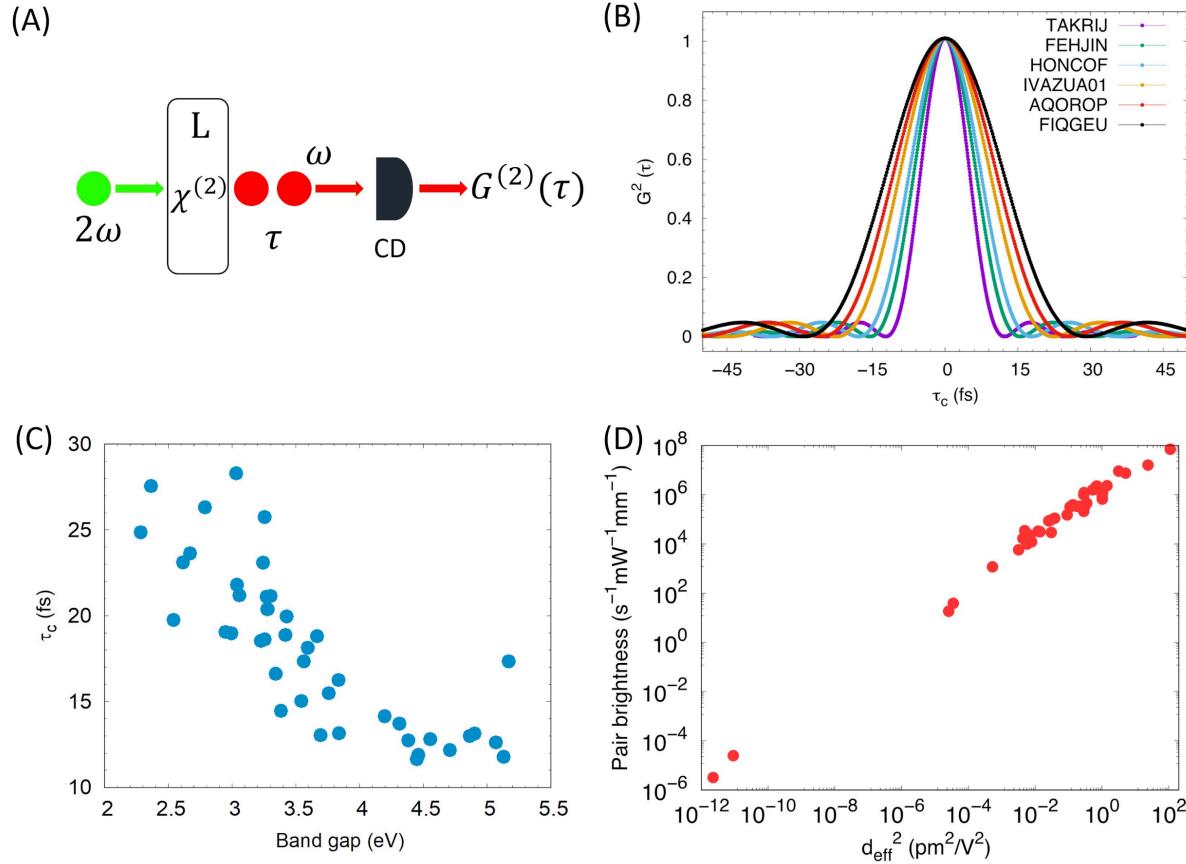


Figure 6. (A) Visible photons (green) are pumped into a NCS MOF single crystal with propagation length L . Entangled photon pairs at half the pump frequency (red), produce from the crystal with a small delay τ . Photon pairs are collected with a coincidence detector (CD), and the delay times are post-processed to give a two-time correlation function $G^{(2)}(\tau)$. (B) $G^{(2)}(\tau)$ of selected MOFs. (C) Entangled photon correlation time as a function of band gap for all the crystals. (D) Pair brightness as a function of d_{eff}^2 .

All the results discussed above are with pump wavelength of 1064 nm. From all the crystals we have used in our study, we could not estimate d_{eff} for QAMFUF01 and BEKVOD crystals although they have high $\chi^{(2)}$ as shown in Figs. S3 and S4, because we were not able to find any phase matching angle at 1064 nm. In order for these crystals to be phase-matchable, we plotted the phase-matching angle as a function of wavelength. Figure 7A shows how θ_m changes with signal wavelength for QAMFUF01 (1600 - 2500 nm) and BEKVOD (2200 - 3200 nm). We then calculated $\chi^{(2)}$ for QAMFUF01 and BEKVOD crystals at 1600 and 2200 nm. Figure 7B shows the d_{eff} of these two crystals at 1600 and 2200 nm.

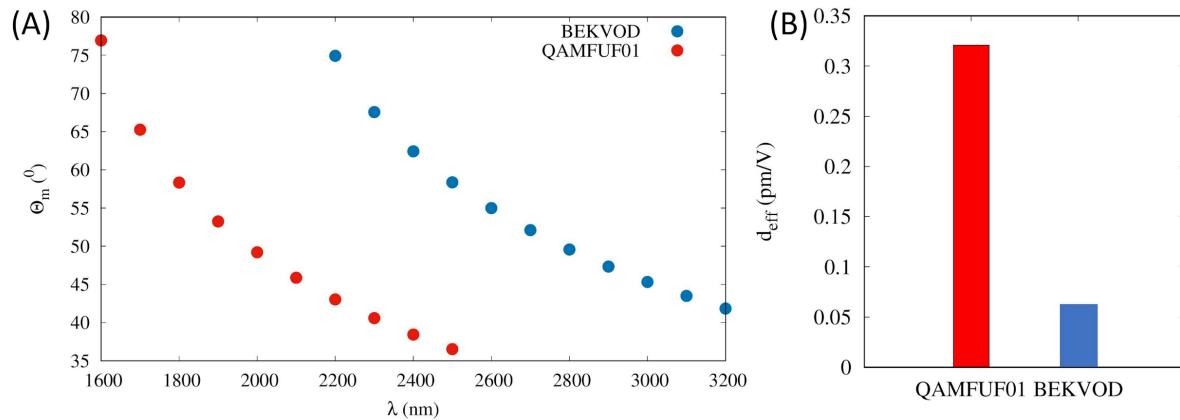


Figure 7. (A) Phase matching angle (θ_m) for QAMFUF01 and BEKVOD crystals for a range of signal wavelengths. (B) Effective nonlinearity (d_{eff}) for QAMFUF01 crystal at 1600 nm and BEKVOD crystal at 2200 nm.

Having nonlinear optical materials to be operational over wider bandwidth is an important requirement for photonics application. We have shown in Table 1 how the photon conversion rate is affected as a function of pump wavelength. We chose MOFTIL because it is the best crystal for entangled photon sources with pair conversion rate of $1.7 \times 10^7 \text{ s}^{-1} \text{ mW}^{-1} \text{ mm}^{-1}$, and birefringence of 0.42 at 1064 nm and band gap of 3.2 eV. We observe that d_{eff} and entangled photon pairs decrease with increasing pump wavelength (decreasing photon energy).

Table 1: d_{eff} , number of entangled photon pairs and photon pair correlation time at different signal wavelength for MOFTIL crystal.

MOF	λ_s (nm)	d_{eff} (pm/V)	R ($\text{s}^{-1} \text{mW}^{-1} \text{mm}^{-1}$)	τ_c (fs)
MOFTIL	909	6.24	31.36×10^6	26.63
	1064	4.88	16.13×10^6	23.66
	1100	4.70	14.32×10^6	23.11
	1546	3.61	5.42×10^6	18.61

In summary, the band gap, birefringence, signal wavelength, phase matching angles, effective non-linearity (contracted form of $\chi^{(2)}$ tensor), number of entangled photons are correlated with each other. Figure 8 shows how all of these quantities are interrelated and how these correlation can be exploited for designing new materials which will be SPDC efficient.

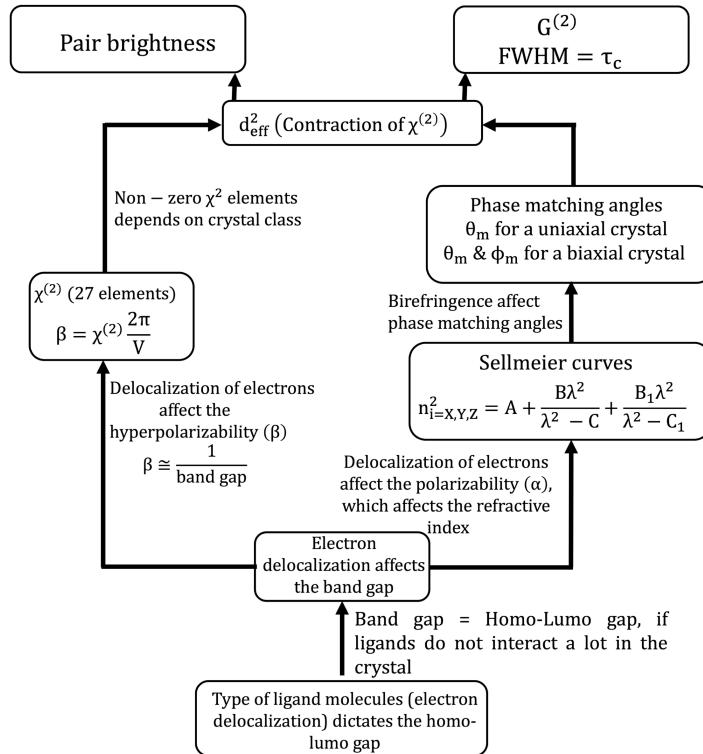


Figure 8. Flowchart showing how different quantities are correlated with each other.

4. Conclusion

We have successfully explored MOF database for mono-ligand MOFs with Zn as a metal center for generating entangled light via collinear degenerate Type-I SPDC. All the MOFs in our database is experimentally synthesized and come from CCDC after applying MOF filter as discussed in the method section. We have systematically developed and implemented a multiscale computational technique to the selected MOFs (uniaxial or biaxial) to identify the features that are important for high brightness and large photon correlation times. We found MOFTIL crystal to be the best candidate entangled photon source with photon conversion rates of 1.7×10^7 pairs s⁻¹ mW⁻¹ mm⁻¹, and birefringence of 0.42 at 1064 nm and band gap of 3.2 eV. We observe that the band gap of the crystals is related to the properties such as birefringence (an important parameter for angle phase matching), effective nonlinearity and the entangled photon pair properties. Band gap can be related to the HOMO-LUMO gap of the ligand, assuming that the ligands do not interact significantly in the crystal, which can be a design criteria for preparing new MOF crystals with desired band gaps. Advanced entangled photon sources are crucial for photonic quantum technology and MOF nonlinear materials show great promise for modern nonlinear applications.

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5. Data and Codes Availability

All the data for Sellmeier curves and second-order susceptibility tensor obtained with CRYSTAL17 are available on GitHub. Codes to calculate phase-matching angles, effective nonlinearity, correlation function and number of entangled photon pairs for Type-I SPDC are available on GitHub. Link to GitHub page is [GitHub-Data-Codes](#).

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7. Supplementary Information

First-Principles Screening of Metal-Organic Frameworks for Entangled Photon Pair Generation

Sanoj Raj^{1,4}, Simón Paiva², Rubén A. Fritz², Felipe Herrera^{2,3}
and Yamil J. Colón¹

¹ Department of Chemical and Biomolecular Engineering, University of Notre Dame, IN 46556, USA

² Department of Physics, Universidad de Santiago de Chile, Av Victor Jara 3493, Santiago, Chile

³ Millennium Institute for Research in Optics, Concepción, Chile

⁴ Current address: Department of Chemistry, Bowdoin College, ME 04011, USA

E-mail: ycolon.nd.edu; felipe.herrera.u@usach.cl

1. Method

Effective non-linearity:

The electric field component in the ordinary axis is given by $E_j^o(\omega) = (a_j)E^o(\omega)$ and the electric field component in the extraordinary axis is given by $E_j^e(\omega) = (b_j)E^e(\omega)$, where,

$$(a_j) = \begin{pmatrix} \sin\phi \\ -\cos\phi \\ 0 \end{pmatrix}, (b_j) = \begin{pmatrix} -\cos\theta\cos\phi \\ -\cos\theta\sin\phi \\ \sin\theta \end{pmatrix}. \quad (1)$$

Uniaxial crystal: For type-I negative uniaxial, d_{eff} is calculated as

$$P_{oo}^e(\omega_3) = b_i d_{ijk}(\omega_3, \omega_2, \omega_1) a_j a_k E_j(\omega_2) E_k(\omega_1), \quad (2)$$

and for a positive uniaxial crystal, we use

$$P_{ee}^o(\omega_3) = a_i d_{ijk}(\omega_3, \omega_2, \omega_1) b_j b_k E_j(\omega_2) E_k(\omega_1), \quad (3)$$

$P(\omega_3)$ is the dielectric polarization of the crystal at the pump frequency $\omega_3 = \omega_1 + \omega_2$ ($\omega_3 = 2\omega$ and $\omega_2 = \omega_1 = \omega$). A conventional *e-oo* type-I condition was used [1] for negative uniaxial crystal, where the entangled signal and idler are polarized along the ordinary axis (*o*) and the pump is polarized along the extraordinary axis (*e*). For a positive uniaxial crystal, a conventional *o-ee* type-I condition was used

Biaxial crystals: To estimate the d_{eff} for biaxial crystals, it is important that the chosen crystallographic axes *a*, *b*, *c* does not differ from the crystallophysical (optical) one (*X*, *Y*, *Z*), for which one of two relations ($n_X > n_Y > n_Z$, or $n_Z > n_Y > n_X$) is necessarily fulfilled [2, 3, 4, 5]. For biaxial crystal, the choice of satisfying relations $n_X > n_Y > n_Z$, or $n_Z > n_Y > n_X$ is actually superfluous [4, 2, 6, 7]. We have satisfied the relation $n_Z > n_Y > n_X$ and necessary transformation of tensor element is done to

calculate the d_{eff} using Eqns. 2 and 3 for negative and positive biaxial crystal. The phase matching direction which gives the maximum d_{eff} among all possible phase matching directions, solving equation 5, is termed the optimum phase matching direction. We use the maximum value of d_{eff} for other analysis.

It is important to note that in order to calculate d_{eff} , we have to know whether the crystal is uniaxial (positive/negative) or biaxial (positive/negative) and what are the phase matching angles (θ_m for uniaxial, θ_m and ϕ_m for biaxial). The difference in the phase matching angle is due to one axis enabling symmetry of revolution in uniaxial crystals compared to biaxial crystals which lack that symmetry. All the discussion about a crystal being positive/negative uniaxial or positive/negative biaxial and their phase matching angle calculations are discussed below. The angles defined are according to the positive nonlinear optics frame convention of Roberts [7].

Positive/negative crystal and Birefringence: The value of birefringence in uniaxial crystal is the difference between $n_o(n_X)$ and $n_e(n_Z)$, $\Delta n = n_o - n_e$. For $n_o > n_e$ ($n_o < n_e$), the material is termed a negative (positive) uniaxial crystals [8, 9]. For materials which are biaxial, the situation is very complex. The three refractive indices n_X , n_Y and n_Z along X, Y and Z axis are different. The semiaxes of the ellipsoid can always be chosen in a way that either $n_Z > n_Y > n_X$ or $n_Z < n_Y < n_X$ is fulfilled [4, 2, 6, 7, 3, 5]. By convention, $n_Z > n_Y > n_X$, we can calculate $n_Z - n_Y > n_Y - n_X$ to decide whether the biaxial crystal is positive or negative. If $n_Z - n_Y > n_Y - n_X$, the material is termed as positive in analogy to uniaxial crystals, and if $n_Z - n_Y < n_Y - n_X$, the material is termed as negative in analogy to uniaxial crystals [8, 9]. It is important to note that through refractive indices, the crystal type (positive/negative) is wavelength (temperature) dependent. In a biaxial crystal, the birefringence is taken to be the difference between maximum (n_Z) and minimum (n_X) refractive index.

Sellmeier curves and Type-I phase matching angle: For the phase matching geometry for different crystals, we are interested in the Sellmeier curves along different axes. We have obtained the Sellmeier curves $n_{i=X,Y,Z}^2(\lambda)$ for all the MOFs crystals from the dielectric tensor $\epsilon_{ij}(\omega)$, computed at wavelength intervals from $\lambda_{\min} = hc/E_g$ to $\lambda_{\max} = 1100$ nm. E_g is the band gap for different MOFs crystals. We fit the Sellmeier curves for each crystal axis to the standard relation

$$n_i^2(\lambda) = A + \frac{B\lambda^2}{\lambda^2 - C} + \frac{B_1\lambda^2}{\lambda^2 - C_1}, \quad (4)$$

to obtain the Sellmeier coefficients.

For a uniaxial crystal, the Type-I phase-matching angle, θ_m , is taken from the optic axis. The phase-matching "point" in three-dimensional form symmetrical cones [10, 1]. We can obtain θ_m for negative uniaxial crystal using $\sin^2(\theta_m) = (n_e^2(2\omega)/n_o^2(\omega))(n_o^2(2\omega) - n_o^2(\omega))(n_o^2(2\omega) - n_e^2(2\omega))$, and for positive uniaxial crystal using $\sin^2(\theta_m) = (n_e^2(\omega)/n_o^2(2\omega))(n_o^2(\omega) - n_o^2(2\omega))/(n_o^2(\omega) - n_e^2(\omega))$ [10].

To calculate the phase matching angles θ_m and ϕ_m in biaxial crystals, one must

solve the following equation for θ and ϕ

$$\frac{k_X^2}{n^{-2} - n_X^{-2}} + \frac{k_Y^2}{n^{-2} - n_Y^{-2}} + \frac{k_Z^2}{n^{-2} - n_Z^{-2}} = 0 \quad (5)$$

where $k_X = \sin\theta \cos\phi$, $k_Y = \sin\theta \sin\phi$, and $k_Z = \cos\theta$. θ is the angle from the Z-axis and ϕ is the angle from the X-axis in the XY plane. n_X , n_Y and n_Z are the three principal refractive indices. Equation 5 can be simplified to equation 6 by letting $x = n^{-2}$, $B = [-k_X^2(b+c) - k_Y^2(a+c) - k_Z^2(a+b)]$, $C = k_X^2bc + k_Y^2ac + k_Z^2ab$, where $a = n_X^{-2}$, $b = n_Y^{-2}$, $c = n_Z^{-2}$

$$x^2 + Bx + C = 0 \quad (6)$$

On solving equation 6, we get

$$n = \sqrt{2}/(\sqrt{-B \pm \sqrt{(B^2 - 4C)}}). \quad (7)$$

For biaxial type-I phase matching, we solve

$$\sqrt{2}/(\sqrt{-B_1 - \sqrt{(B_1^2 - 4C_1)}}) = \sqrt{2}/(\sqrt{-B_2 + \sqrt{(B_2^2 - 4C_2)}}), \quad (8)$$

where the subscripts 1 and 2 stand for fundamental and second harmonic wavelengths. On solving Eq. 8, we get θ and ϕ for biaxial type-I phase matching. More details about type-I phase-matching in biaxial crystal are given by Yao and Fahlen [3].

Glauber Correlation function: The arrival times for all the photon pairs emitted by the crystal are detected in a coincidence setup and the probability of detecting two-photon pairs at different times t_1 and t_2 are proportional to the correlation function $G^{(2)}(t_1, t_2)$ given by

$$G^{(2)}(t_1, t_2) = |\langle 0 | \left(\hat{E}^{(-)}(t_2) \hat{E}^{(+)}(t_1) \right) | \Psi_2 \rangle|^2 \quad (9)$$

where the electric field operators are given by

$$E^{(+)}(r, t) = \frac{1}{\sqrt{V}} \sum_{k, \sigma} e_{k, \sigma} \epsilon_{k, \sigma} \alpha_{k, \sigma} G(\omega) \exp[i(k \cdot r - \omega t)] = [E^{(-)}(k, t)]^* \quad (10)$$

where the index σ is summed over a two-dimensional orthogonal polarization vector. ϵ_0 is the free space permittivity, $G(\omega)$ is a transmission function that models the detector filter, V is the quantization volume, k is an index summed over all wave vectors, $e_{k, \sigma}$ is the two-dimensional unit polarization vector, ω the frequency and $\alpha_{k, \sigma}$ is the mode amplitude.

We assume that this correlation depends only on a relative time $\tau = t_1 - t_2$. This can be done because we are only considering the pump as a Gaussian beam and the Hermite-Gauss basis for the two generated photons. In other words, there is not a spatial dependency for the correlation assuming a Hermite-Gauss basis for the generated photons. The right-hand side of Eq. (9) is proportional to the frequency spectrum of the light as

$$G^{(2)}(\tau) \propto |I_0(\tau)|^2 \quad (11)$$

and the frequency spectrum of the light is given by:

$$I_0(\tau) = \int_{-\infty}^{\infty} d\nu \Phi\left(\frac{\Delta k L}{2}\right) e^{-\left(\frac{v^2}{\sigma^2}\right)} e^{-i\nu\tau} \quad (12)$$

where ν is a small detuning frequency and $\Phi(x)$ is known as the joint spectral function (JSA), that is typically proportional to a "sinc" function. Δk is given by

$$\Delta k \approx \left(\frac{n_g}{c}\right) \left(\omega_s - \frac{\omega_p}{2}\right) + \kappa \left(\omega_s - \frac{\omega_p}{2}\right)^2 \quad (13)$$

where n_g is the difference between the group velocity for the two photons generated and κ correspond to the group velocity dispersion of the generated photon. In this case as we are interested in Type I degenerate SPDC, this means that the two generated photons have the same central frequency that is half the central frequency of the pumped photon. The n_g is zero because the two generated photons have the same polarization and so the expression for Δk is

$$\Delta k \approx \frac{\kappa\nu^2}{4} \quad (14)$$

where ν correspond to a small detuning frequency.

Combining the equations 12 and 14 in equation 15, we obtain that the expression for the Glauber Correlation function is

$$G^{(2)}(\tau) \propto \left| \int_{-\infty}^{\infty} d\nu \text{sinc}\left(\frac{\kappa\nu^2 L}{4}\right) e^{-\left(\frac{v^2}{\sigma^2}\right)} e^{-i\nu\tau} \right|^2 \quad (15)$$

Counting Rate: The biphoton generation rate depends on the overlap integral

$$|\Phi(\Delta k_z)|^2 \equiv \left| \int d^3r (\chi_{eff}^2(\vec{r}) G_p^*(\vec{r}) g_{\vec{\mu}_1}(x, y) g_{\vec{\mu}_2}(x, y) e^{-i\Delta k_z z}) \right|^2 \quad (16)$$

The simplest case to solve is that of the collimated Gaussian pump beam incident on an isotropic rectangular crystal of dimensions $L_x \times L_y \times L_z$ centered at the origin of a Cartesian coordinate system with \hat{z} pointing along the optic axis. If we make the additional assumption that we are collecting the down-converted light into single-mode fibers, then only the photons generated in the zeroth-order Hermite–Gaussian modes will contribute to the rate of detected events. In this case, $G_p(\vec{r})$, $g_{\vec{\mu}_1}$, and $g_{\vec{\mu}_2}$ are all Gaussian functions, so that $|\Phi(\Delta k_z)|^2$ becomes

$$|\Phi(\Delta k_z)|^2 = C_1 \left| \int_{L_z/2}^{-L_z/2} dz e^{-i\Delta k_z z} \right|^2 \left| \int dx dy e^{-\left[(x^2 y^2)\left(\frac{1}{4\sigma_p^2} + \frac{2}{4\sigma_1^2}\right)\right]} \right|^2, \quad (17)$$

where $C_1 = \left(\frac{\chi_{eff}^{(2)}}{2\pi\sigma_1^2}\right)^2$. We assume that the filters for both detectors have the same bandwidth $\sigma_1 = \sigma_2$. To make the limits of the integral over x and y arbitrarily large, it only suffices that the transverse width of the crystal is larger than the dimensions of both the Gaussian pump beam and of the signal and idler modes. Moreover, in single-mode nonlinear waveguides, light can be confined to a much smaller beam diameter

without diverging. With these assumptions, the overlap integral simplifies significantly to

$$|\Phi(\Delta k_z)|^2 = (2\chi_{\text{eff}}^2 L_z)^2 \text{sinc}^2\left(\frac{\Delta k_z L_z}{2}\right) \left| \frac{\sigma_p^2}{\sigma_1^2 + 2\sigma_p^2} \right|^2. \quad (18)$$

Now we can have an expression for the total rate for down-conversion, R , using as a Gaussian beam the pump beam into another Gaussian signal-idler mode, in terms of the signal and idler frequencies ω_1 and ω_2 as

$$R = \int d\omega_1 d\omega_2 C_2 \omega_1 \omega_2 \delta(\Delta\omega) \text{sinc}^2\left(\frac{\Delta k_z L z}{2}\right) \quad (19)$$

Where $C_2 = \frac{|E_p^0|^2 (d_{\text{eff}})^2 L_z^2}{2\pi c^2} \frac{n_{g1} n_{g2}}{n_1 n_2} \left| \frac{\sigma_p^2}{\sigma_1^2 + 2\sigma_p^2} \right|^2$. From energy conservation we have

$$\omega_p = \omega_1 + \omega_2. \quad (20)$$

Now we can integrate over one of the frequencies using the delta function, in this case we integrate over the frequency ω_2 getting

$$R = C_2 \int d\omega_1 \omega_1 (\omega_p - \omega_1) \text{sinc}^2\left(\frac{\Delta k_z L z}{2}\right) \quad (21)$$

where the phase matching function is given by

$$\Delta k_z = k(\omega_1) + k(\omega_p - \omega_1) - k(\omega_p). \quad (22)$$

This function is analogous to the expression of equation 13, meaning that in the case of type I SPDC we need to replace Δk for this expression.

Estimation of HOMO-LUMO gap: To calculate the HOMO-LUMO gap for every ligand in every MOF, first, we retrieve the chemical name of the organic molecules from the chemical name of the MOFs in the Cambridge Structural Database (CSD) [11]. By using conventional inorganic compound naming we were able to filter and obtain the chemical name of the ligand for Zinc based MOFs with one organic molecule as ligand and Zn^{2+} as node. Using OPSIN [12] we converted these names to SMILES and posteriorly with Rdkit [13]. We generated a 3D structure for every molecule and subsequently perform geometry optimization of the coordinates with Dmol3 [14] with Minnesota functional and DNP 4.4 basis set of Dmol3 and obtain the values for highest occupied molecular orbital and the lowest unoccupied molecular orbital, these values are used to estimate the HOMO-LUMO gap. A more refined approximation would be to extract the coordinates of the ligands from the crystal but a correct capping of each ligand is required to represent the correct valence. This chemical name-to-structure approach requires precise chemical naming on the databases, as misspelled or bad labeling is possible.

2. Biaxial and Uniaxial MOF properties

Table 1: Crystal system, crystal class, space group, band gap, coordinate transformation, birefringence and crystal type for biaxial crystals and that N is for negative and P is for positive.

MOFs	Crystal system	Crystal Class	Space group	Band gap (eV)	Transformation	Birefringence (1064 nm)	Crystal type
SOMNUG	Triclinic	1	P1	2.788	x, y, z -> a, b, c	0.467967	N
RATDAS01	Monoclinic	2	P21	4.3819	x, y, z -> a, c, b	0.06553	P
TAKRIJ	Monoclinic	2	P21	4.4618	x, y, z -> a, c, b	0.102171	P
FIPWUY	Monoclinic	2	P21	4.1972	x, y, z -> b, a, c	0.117632	N
LASPZN	Monoclinic	2	P21	3.6932	x, y, z -> a, b, c	0.116657	P
FIRZIP	Monoclinic	2	P21	3.3416	x, y, z -> a, c, b	0.042447	P
PODREH	Monoclinic	2	C2	2.6703	x, y, z -> b, c, a	0.281457	N
RUVBAN	Monoclinic	2	C2	3.2442	x, y, z -> c, a, b	0.325459	N
OFUWIV	Monoclinic	2	C2	5.0703	x, y, z -> b, c, a	0.144579	P
MUYGOE	Monoclinic	2	C2	3.836	x, y, z -> b, a, c	0.09256	N
NELWUY	Monoclinic	2	C2	4.4495	x, y, z -> b, c, a	0.038723	N
AQOROP	Monoclinic	m	PC	2.3644	x, y, z -> c, b, a	0.647674	N
KOMMII	Monoclinic	m	PC	5.1303	x, y, z -> a, b, c	0.04897	P
MOFTIL	Monoclinic	m	PC	3.2545	x, y, z -> c, b, a	0.422821	N
ECIWAO	Monoclinic	m	CC	2.2834	x, y, z -> b, a, c	0.372085	P
IDOGIR	Monoclinic	m	CC	4.8648	x, y, z -> c, b, a	0.085201	N
RUBDOI	Monoclinic	m	CC	3.4187	x, y, z -> c, b, a	0.152212	N
SEYVIC	Monoclinic	m	CC	4.3136	x, y, z -> b, c, a	0.145033	P
ECIHIK	Orthorhombic	222	P21212	3.8375	x, y, z -> c, a, b	0.145033	P
ODIVON	Orthorhombic	222	P21212	3.429	x, y, z -> c, a, b	0.138952	N
WOVPAB	Orthorhombic	222	P21212	2.5401	x, y, z -> a, c, b	0.115771	N
DOYBEY	Orthorhombic	222	P212121	3.6675	x, y, z -> c, b, a	0.111669	N
EWUSIZ	Orthorhombic	222	P212121	4.5544	x, y, z -> c, b, a	0.091731	P
JUKVEQ02	Orthorhombic	222	P212121	2.9487	x, y, z -> c, a, b	0.080823	N
NIBRUN	Orthorhombic	222	P212121	3.2788	x, y, z -> a, b, c	0.215102	P
NIBSAU	Orthorhombic	222	P212121	3.277	x, y, z -> a, b, c	0.215102	P
VAHWOS01	Orthorhombic	222	P212121	3.2556	x, y, z -> a, b, c	0.683581	P
WOVPEF	Orthorhombic	222	P212121	2.9953	x, y, z -> c, a, b	0.040637	N
XISBUX	Orthorhombic	222	P212121	4.9015	x, y, z -> b, c, a	0.072898	N
HONCOF	Orthorhombic	mm2	PCA21	3.5635	x, y, z -> a, b, c	0.14768	P
DIFKOS	Orthorhombic	mm2	PCA21	5.1694	x, y, z -> b, a, c	0.021875	P
FEHJIN	Orthorhombic	mm2	PCA21	3.5443	x, y, z -> b, c, a	0.203427	P
VEKNEH	Orthorhombic	mm2	PNA21	3.7591	x, y, z -> b, a, c	0.091819	P
IVAZUA01	Orthorhombic	mm2	PNA21	3.0381	x, y, z -> a, b, c	0.227767	N
FIQGEW	Orthorhombic	mm2	ABA2	3.0333	x, y, z -> a, c, b	0.318939	N
NUYWUA	Orthorhombic	mm2	ABA2	3.2267	x, y, z -> b, c, a	0.166632	P
OXUNUR	Orthorhombic	mm2	FDD2	2.6149	x, y, z -> c, a, b	0.31352	N

Table 2: Crystal system, crystal class, space group, band gap, coordinate transformation, birefringence and crystal type for uniaxial crystals. npm stands for no phase matching.

MOFs	Crystal system	Crystal class	space group	Band gap (eV)	Coordinate assignment	Crystal type	Birefringence	θ_m	d_{eff} (pm/V)
VURQEF	Tetragonal	422	P4122	3.2709	X, Y, Z → a, b, c	N	0.2916	23.67	0
ONOCOL01	Tetragonal	422	P41212	3.1801	X, Y, Z → a, b, c	N	0.0085	npm	
DIXWAJ	Tetragonal	422	P43212	3.3833	X, Y, Z → a, b, c	N	0.0588	42.19	0
EGIKUB02	Tetragonal	422	P43212	3.3028	X, Y, Z → a, b, c	P	-0.2115	27.78	0
HICDUV	Tetragonal	422	P43212	2.6224	X, Y, Z → a, b, c	P	-0.0826	npm	
IMIDZB01	Tetragonal	4mm	I41CD	4.6497	X, Y, Z → a, b, c	P	-0.0253	npm	
JETVOW	Hexagonal	32	P3121	2.5202	X, Y, Z → a, b, c	P	-0.0454	npm	
SAQFUM	Tetragonal	-42m	I-42D	3.5932	X, Y, Z → a, b, c	N	0.0924	41.91	0.1
HUTZAX01	Hexagonal	32	P3221	3.0568	X, Y, Z → a, b, c	P	-0.1065	48.33	1.18
QAMFUF01	Hexagonal	32	P3221	2.3881	X, Y, Z → a, b, c	P	-0.0355	npm	
BEKVOD	Trigonal	-3m1	R3C	3.5104	X, Y, Z → a, b, c	P	-0.0095	npm	
WUJFOW	Hexagonal	6	P61	4.7085	X, Y, Z → a, b, c	N	0.0266	59.76	0.11

3. Biaxial crystal Phase-matching angle (θ , ϕ)

3.1. Test Case BiBO and KTP

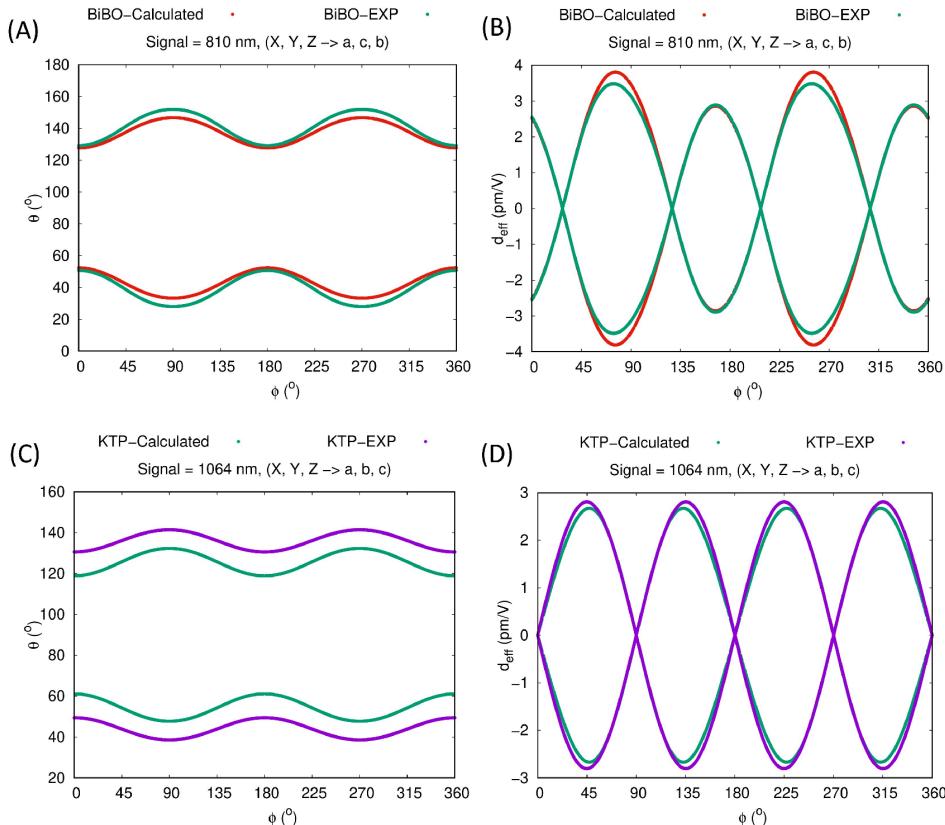


Figure 1. (A) Experimental [5] and calculated phase-matching angles for BiBO crystal belonging to crystal class 2. (B) d_{eff} of BiBO crystal belonging to crystal as a function of phase matching angle, θ . (C) Experimental [3] and calculated phase-matching angles for KTP crystal belonging to crystal class mm2. (B) d_{eff} of KTP crystal belonging to KTP crystal as a function of phase matching angle, ϕ . θ is not shown for clarity

3.2. Biaxial crystals used in our study

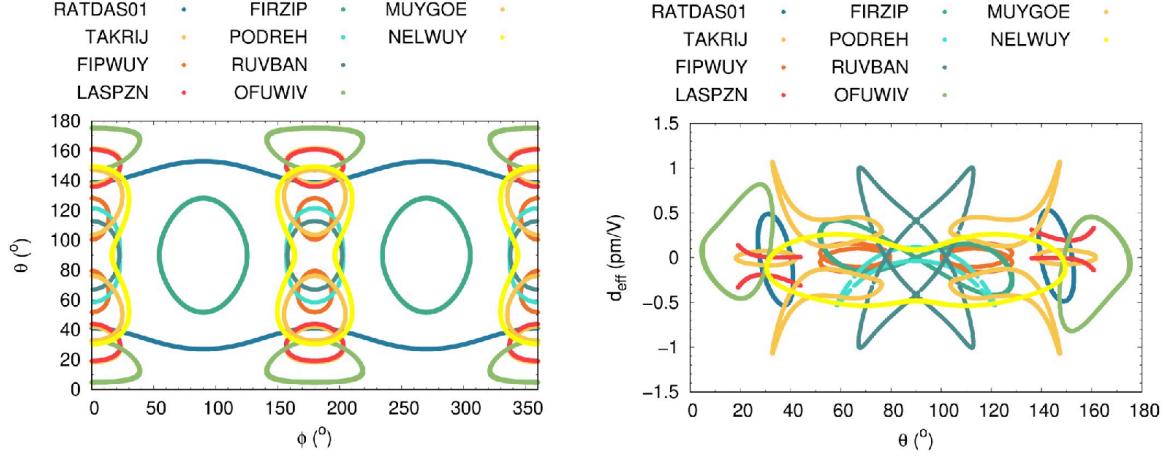


Figure 2. (Left) Phase-matching angle for MOF crystal belonging to crystal class 2. (Right) d_{eff} of crystals belonging to crystal class 2 as a function of phase matching angle, θ . ϕ is not shown for clarity

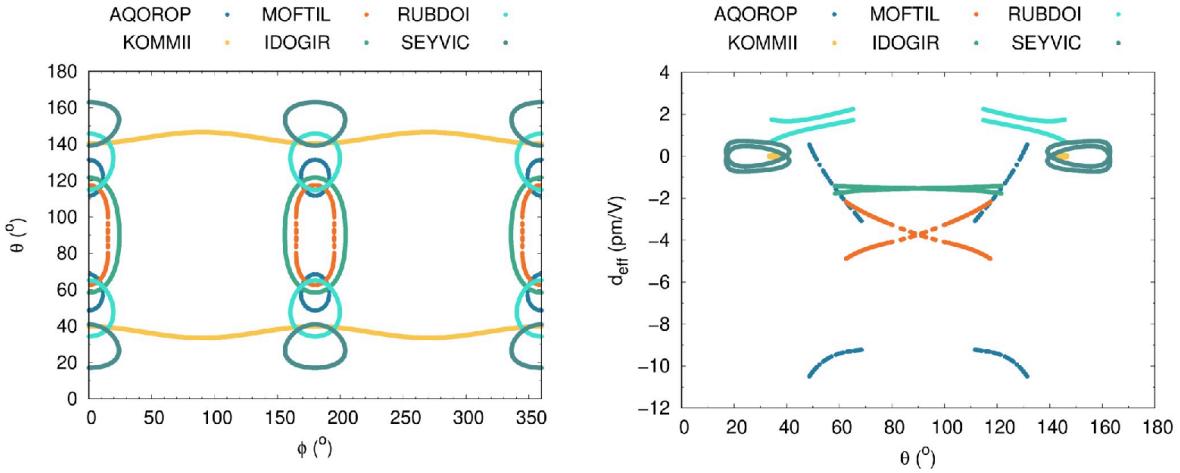


Figure 3. (Left) Phase-matching angle for MOF crystal belonging to crystal class m. (Right) d_{eff} of crystals belonging to crystal class m as a function of phase matching angle, θ . ϕ is not shown for clarity

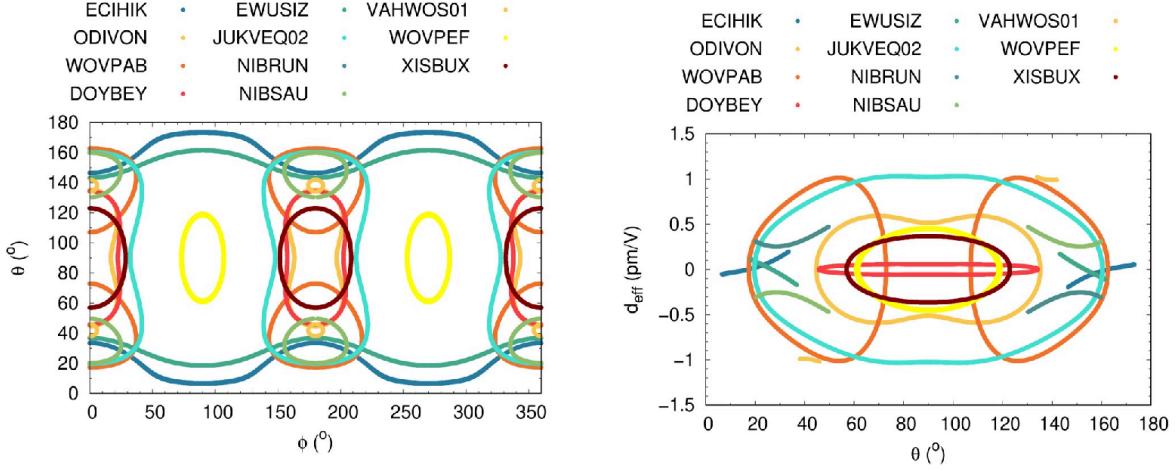


Figure 4. (Left) Phase-matching angle for MOF crystal belonging to crystal class 222. (Right) d_{eff} of crystals belonging to crystal class 222 as a function of phase matching angle, θ . ϕ is not shown for clarity

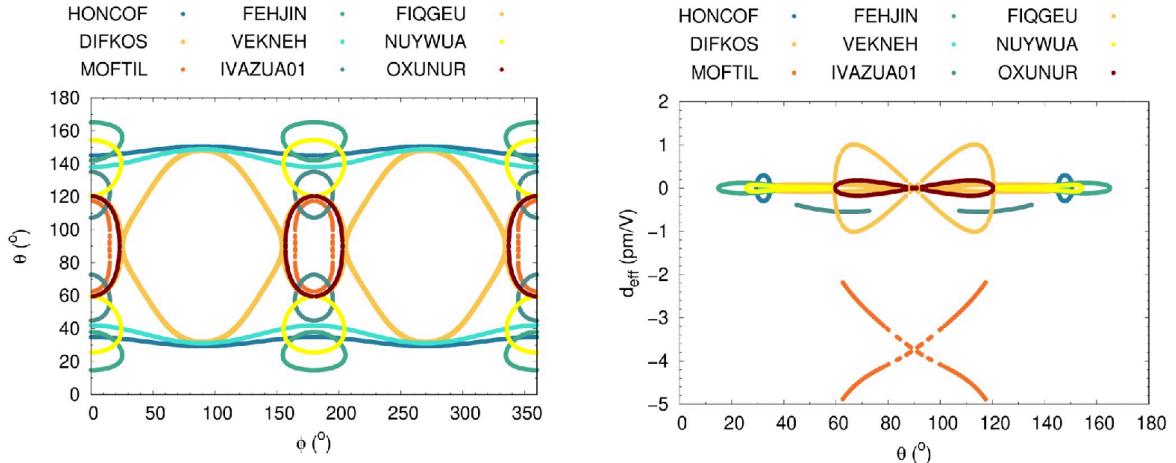


Figure 5. (Left) Phase-matching angle for MOF crystal belonging to crystal class mm2. (Right) d_{eff} of crystals belonging to crystal class mm2 as a function of phase matching angle, θ . ϕ is not shown for clarity

4. Second-order nonlinear susceptibility tensor ($\chi^{(2)}$)

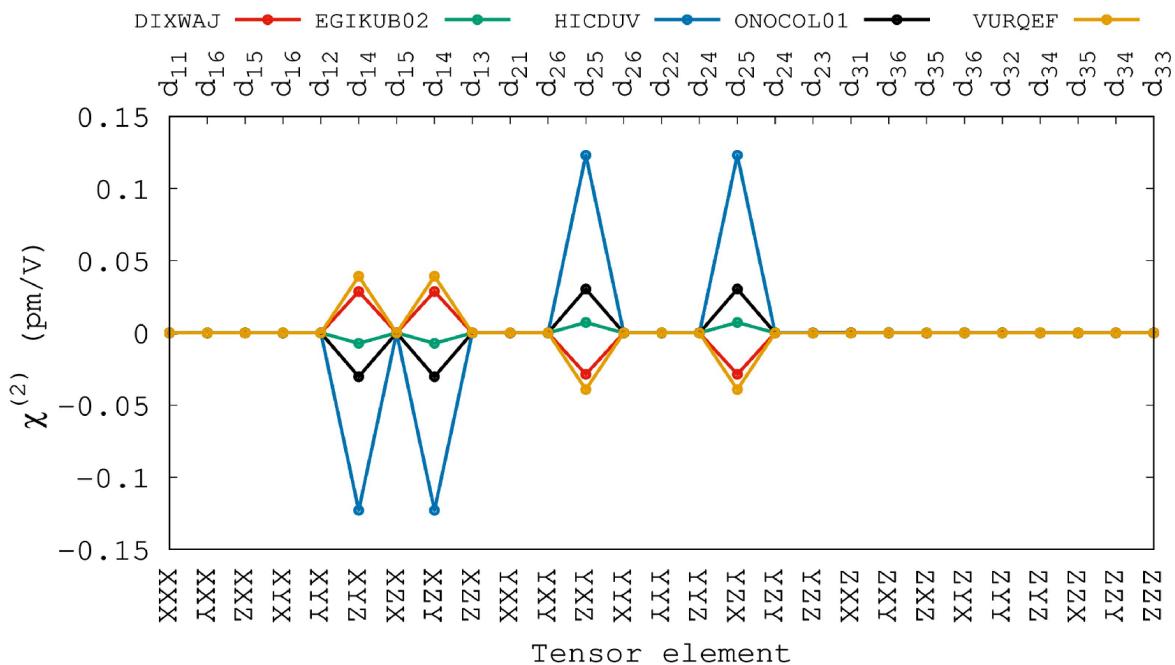


Figure 6. $\chi^{(2)}$ of different MOF crystal belonging to crystal class 422.

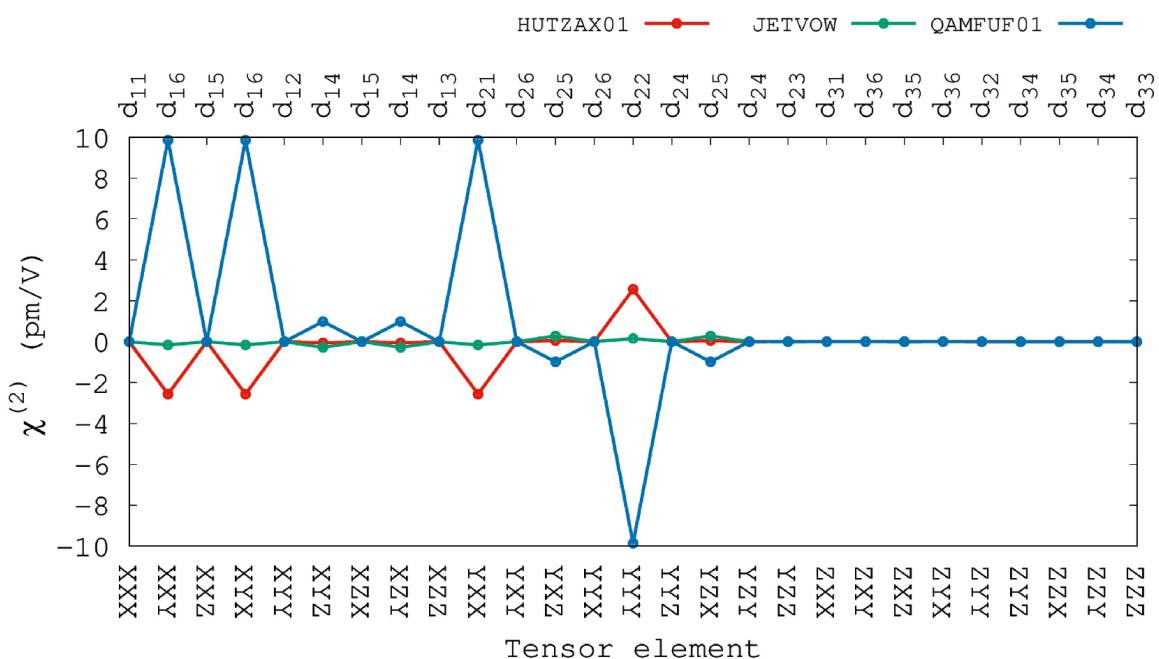


Figure 7. $\chi^{(2)}$ of different MOF crystal belonging to crystal class 32.

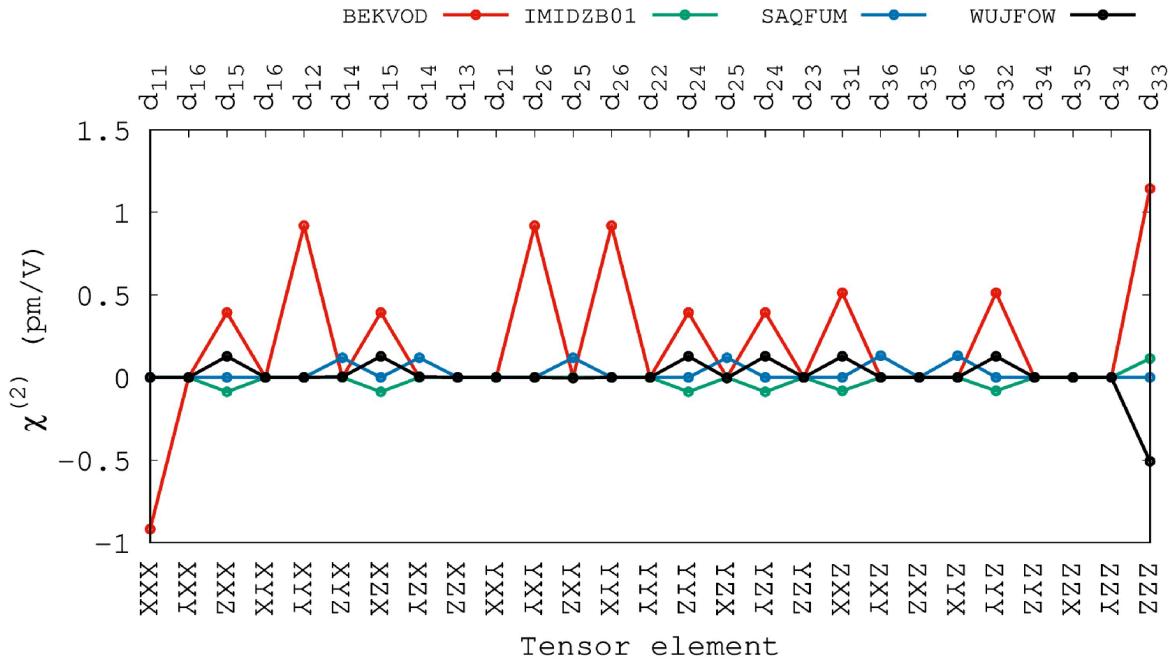


Figure 8. $\chi^{(2)}$ of different MOF crystal belonging to crystal class -3m1, 4mm, -42m and 6.

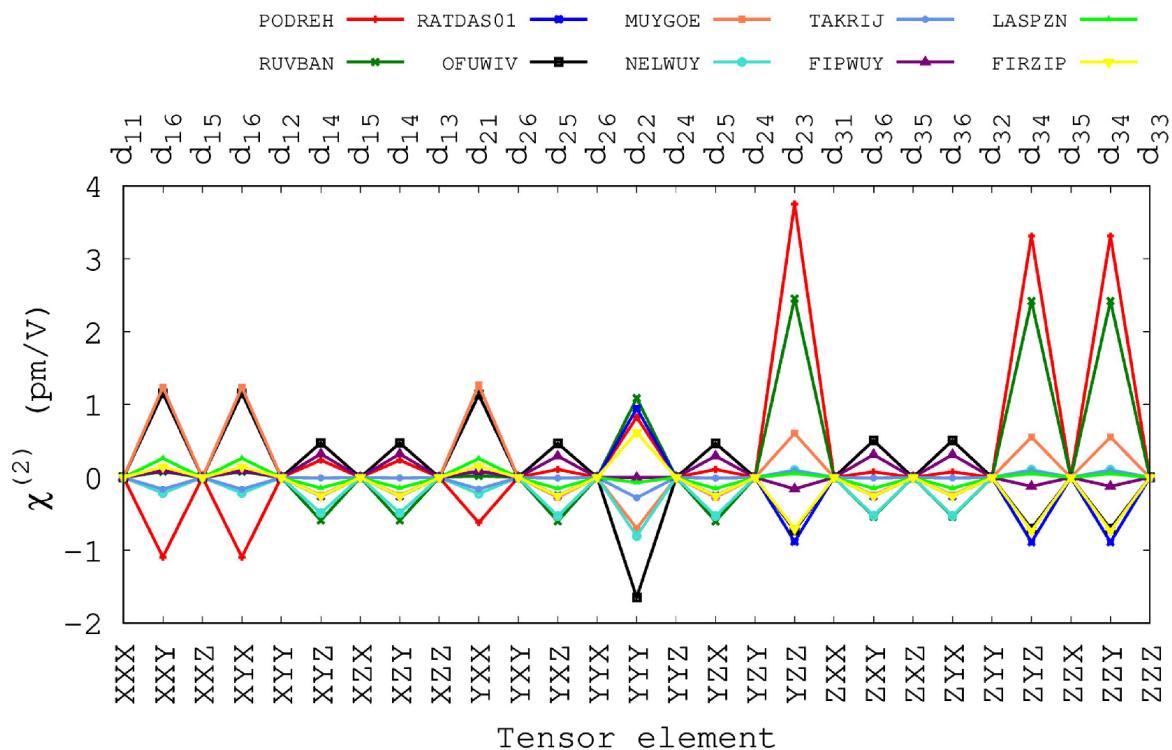


Figure 9. $\chi^{(2)}$ of different MOF crystal belonging to crystal class 2.

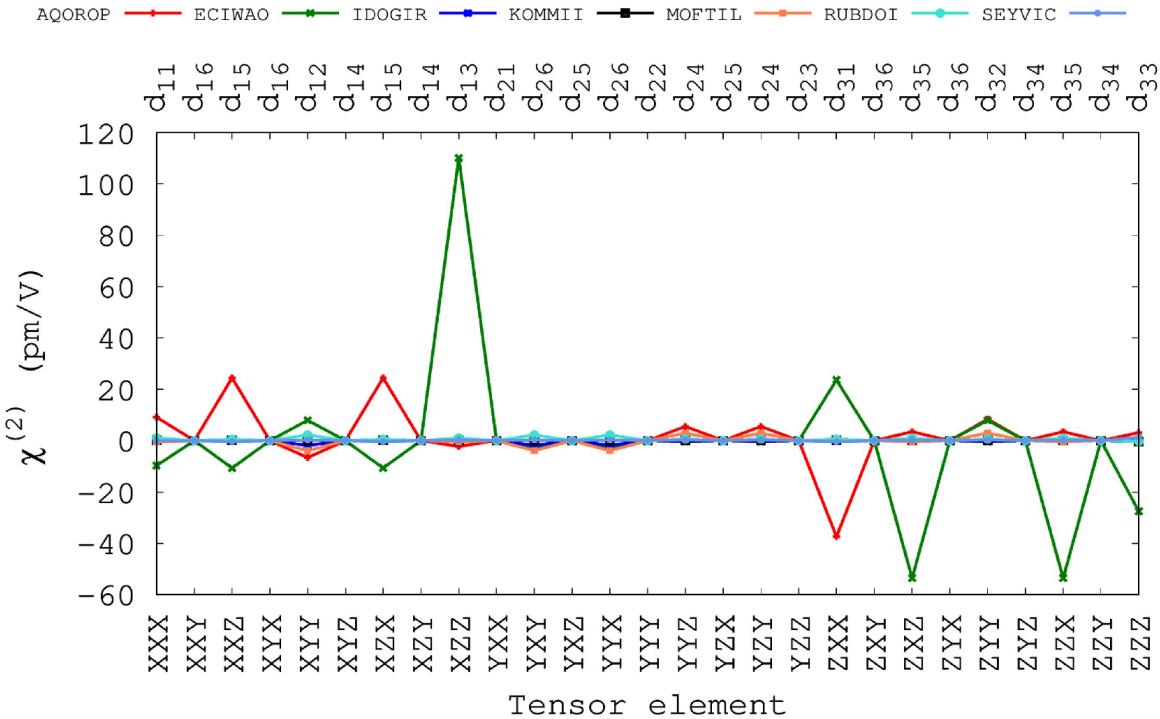


Figure 10. $\chi^{(2)}$ of different MOF crystal belonging to crystal class m.

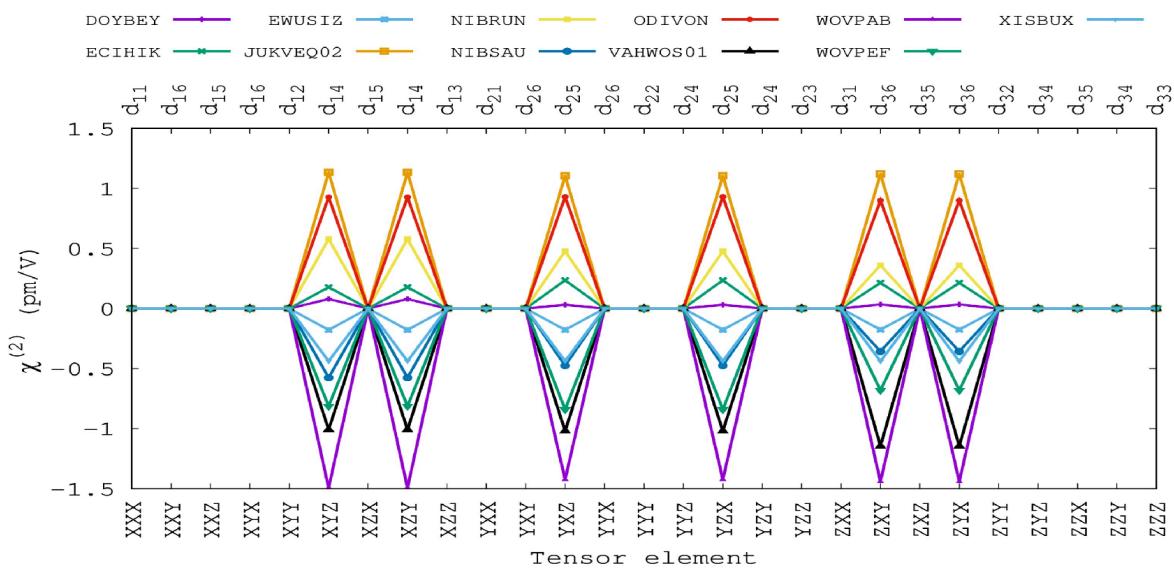


Figure 11. $\chi^{(2)}$ of different MOF crystal belonging to crystal class 222.

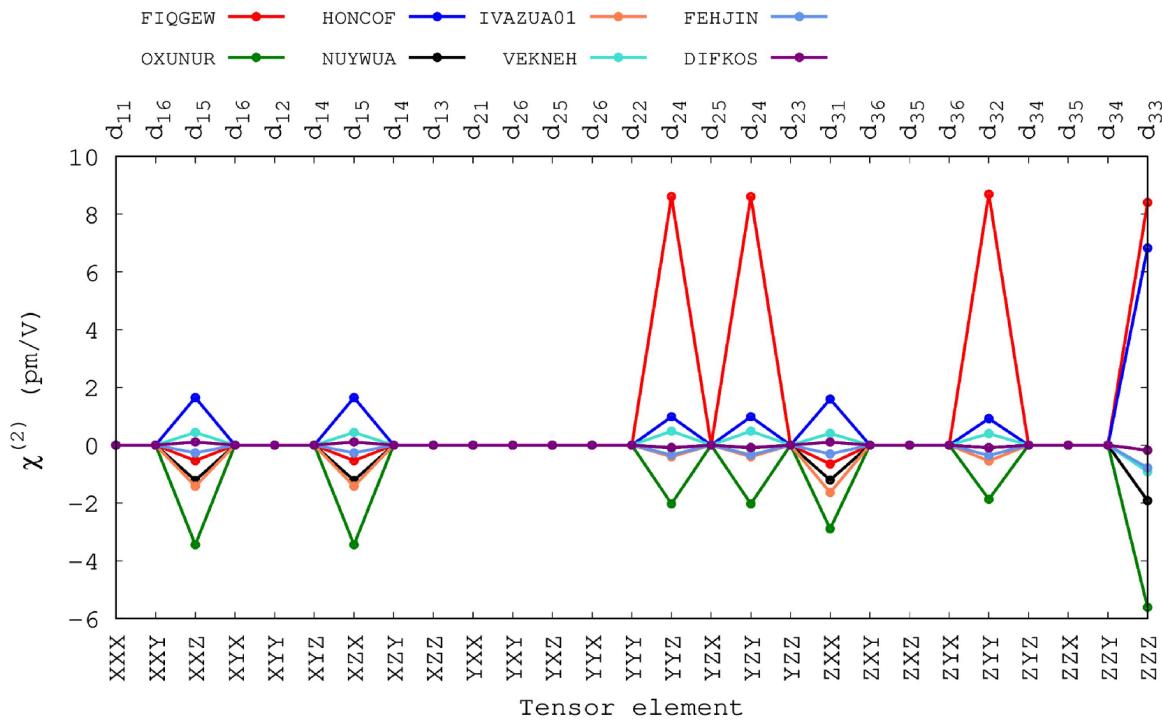


Figure 12. $\chi^{(2)}$ of different MOF crystal belonging to crystal class mm2.

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