Engineering Entangled Photon Pairs with Metal-Organic Frameworks

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The discovery and design of new materials with competitive optical frequency conversion efficiencies can accelerate the development of scalable photonic quantum technologies. Metal-organic framework (MOF) crystals without inversion symmetry have shown potential for these applications, given their nonlinear optical properties and the combinatorial number of possibilities for MOF self-assembly. In order to accelerate the discovery of MOF materials for quantum optical technologies, scalable computational assessment tools are needed. We develop a multi-scale methodology to study the wavefunction of entangled photon pairs generated by selected non-centrosymmetric MOF crystals via spontaneous parametric down-conversion (SPDC). Starting from an optimized crystal structure, we predict the shape of the $G(2)$ intensity correlation function for coincidence detection of the entangled pairs, produced under conditions of collinear type-I phase matching. The effective nonlinearities and photon pair correlation times obtained are comparable to those available with inorganic crystal standards. Our work thus provides fundamental insights into the structure-property relationships for entangled photon generation with metal-organic frameworks, paving the way for the automated discovery of molecular materials for optical quantum technology.

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Engineering entangled photon pairs with metal-organic frameworks

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Abstract

The discovery and design of new materials with competitive optical frequency conversion efficiencies can accelerate the development of scalable photonic quantum technologies. Metal-organic framework (MOF) crystals without inversion symmetry have shown potential for these applications, given their nonlinear optical properties and the combinatorial number of possibilities for MOF self-assembly. In order to accelerate the discovery of MOF materials for quantum optical technologies, scalable computational assessment tools are needed. We develop a multi-scale methodology to study the wavefunction of entangled photon pairs generated by selected non-centrosymmetric MOF crystals via spontaneous parametric down-conversion (SPDC). Starting from an optimized crystal structure, we predict the shape of the $G^{(2)}$ intensity correlation function for coincidence detection of the entangled pairs, produced under conditions of collinear type-I phase matching. The effective nonlinearities and photon pair correlation times obtained are comparable to those available with inorganic crystal standards. Our work thus provides fundamental insights into the structure-property relationships for entangled photon generation with metal-organic frameworks, paving the way for the automated discovery of molecular materials for optical quantum technology.

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I. INTRODUCTION

Optical communication and information technology that exploit the quantum properties of light for enhanced performance [1], has enabled the development of quantum-secure communication networks [2, 3], fault-tolerant quantum computing [4], and quantum sensing devices [5]. In quantum-enhanced applications, the theoretical performance limits can often be related to the quality of the underlying materials used in the implementation of a target protocol. The challenge for materials science is thus being able to tailor the conventional device development workflow such that the performance limits of specific quantum-enhanced protocols can be improved. For example, in several device-independent quantum key distribution protocols, the secure bit rate can be directly related to the flux of entangled photon pairs that can be generated in a nonlinear optical crystal subject to laser driving [6, 7], given a detection efficiency. The generation of entangled photon pairs via down-frequency conversion can in turn be mapped directly into a search for highly crystalline birefringent materials with large second-order nonlinearities, which can be used as entangled photon sources with high brightness [8].

Optical quantum technologies have growing applications in enhanced imaging [9], secure communication [10], and quantum computing [11]. However, the prospects for expanding the reach of quantum-enhanced optical devices is limited, as the number of optical materials that are suitable for advanced protocols is relatively small [12]. For instance, inorganic crystals such as BaB$_2$O$_4$ (BBO) or KH$_2$PO$_4$ (KDP) are widely used for classical and quantum
frequency conversion via three-wave mixing [13]. The optical anisotropy and large secondorder nonlinear susceptibility of these materials in the visible and near infrared, are exploited for spontaneous parametric down-conversion (SPDC) [14], a quantum optical process in which a single pump photon at frequency $\omega$ splits into two indistinguishable photons at $\omega/2$. The indistinguishability of the down-converted photons leads to entanglement of their degrees of freedom [8]. Photon pairs that are entangled in frequency [8], polarization [15], or spatial mode profile [16], are the building blocks of several quantum imaging and secure communication protocols [17].

Metal organic frameworks (MOFs) are emerging materials for applications in nonlinear optics [12, 14, 18, 19]. Recent experimental reports of competitive second-order [20–22] and third-order optical nonlinearities [23] with polycrystalline MOF crystals, have stimulated the need to develop a computational methodology that is capable of screening the available MOF databases, and generate a list of leading candidate structures with a suitable combination of features in their linear and nonlinear optical responses that make them competitive materials for applications in quantum optics. Large-scale computational MOF screening methods for applications in gas storage and gas separation have been developed [24, 25], but extensions of these techniques are needed to discover novel applications of MOF materials in quantum technology.

In this work, we focus on selected non-centrosymmetric MOF crystals assembled from $d^{10}$ transition metal ions (e.g., Zn$^{2+}$, Cd$^{2+}$) as metal nodes, and pyridil-tetrazole (ptz) molecules as organic linkers. Due to the closed $d$-shell of the metal node, and the high HOMO-LUMO gap of the pyridil-tetrazole ligands [26, 27], the MOF crystals that we study are transparent throughout the visible spectrum up to the mid-infrared regime. For the MOF structures considered, the lack of inversion symmetry of their unit cells has enabled the observation of second-harmonic generation (SHG), the up-conversion process that is inverse to SPDC, in polycrystalline powder samples with particle size in the range of microns [18].

In Fig. 1, we illustrate the qualitative behavior of the SHG signal intensity ($I_{\text{SHG}}$) at frequency $2\omega$ upon illumination with a strong laser at frequency $\omega$ of a polycrystalline slab of non-centrosymmetric particles with propagation length $L$ (panel a), and a single non-centrosymmetric crystal of equivalent propagation dimensions (panel b). For a powder sample, propagating optical waves sample an entire distribution of crystal orientations, defined by the direction of the optical axis of individual crystallites relative to the propagation
FIG. 1: Second harmonic generation (SHG) process $\omega \rightarrow 2\omega$ with a nonlinear crystal slab. (a) Polycrystalline slab with propagation length $L$ composed by an ensemble of randomly oriented crystal particles. (b) Single crystal slab with well-defined orientation of the optical $c$-axis. (c) SHG intensity (log scale) as a function of the propagation length $L$ (in units of pump wavelength $\lambda$), for polycrystalline and single-crystal slabs.

light direction. This is the typical condition in SHG tests carried out with MOFs [18]. In this case, the SHG intensity scales linearly with $L$ [28, 29]. For crystals support conditions of perfect phase matching (PPM) [13], this linear $L$-scaling is a suboptimal consequence of the random crystal orientation in the medium. In contrast, for a single crystal with same length $L$, the SHG intensity scales as $L^2$. In other words, the same nonlinear material at the same operating wavelengths has a superior output brightness in a second-order optical process when used as a single crystal. The phase coherence of the waves involved is also superior in single crystals. Figure 1c shows that is not a critical issue for imaging and spectroscopy applications based on second-harmonic generation, which are typically used to study mono-
layers and interfaces with thickness $L$ much smaller than the laser pump wavelength $\lambda$ [30, 31]. This quadratic scaling is beneficial for quantum nonlinear optical processes, such as SPDC, for two main reasons: (i) to maximize the brightness of the non-classical signal (number of entangled photon pairs) and; (ii) to optimize the degree of temporal correlations in coincidence detection (photon indistinguishability), which leads to the entanglement of photonic degrees of freedom [32]. None of these can be achieved using randomly oriented nonlinear crystal powders.

Growing large single crystal MOFs with millimeter dimensions is an experimental challenge. Few groups have reported large centrosymmetric crystals for applications in solid-phase chromatography [33, 34]. As crystal engineering techniques for MOFs continue to improve [35], we present here the first multi-scale computational design methodology for assessing the entanglement properties of near-infrared entangled photon pairs produced via SPDC in a large non-centrosymmetric single crystal MOF under strong laser pumping. We carry out a detailed analysis of three transparent, non-centrosymmetric, birefringent MOFs having the same ptz ligand in their structure: Zn(3−ptz)$_2$ (MIRO-101, CSD: 184958), [Zn(H$_2$O)$_6$]NO$_3$2(3−ptz) (MIRO-102, CSD: 184132) and CdN$_3$(3−ptz)$_2$ (MIRO-103, CSD: 184133). Efforts to grow high-quality single crystals of these MOF species for applications in optics are currently underway [26, 27].

II. RESULTS

A. Methodological Overview

Starting from its optimized crystal structure, we compute the two-time intensity correlation function $G^{(2)}(\tau)$ for coincidence detection of entangled photon pairs generated via SPDC by a non-centrosymmetric MOF subject to strong laser pumping. The multi-scale calculation procedure we propose to achieve this, is described in detail in the Supplementary Material (SM). Briefly, we use solid state DFT within the Coupled Perturbed Hartree-Fock/Kohn-Sham method (CPHF/KS) [36–38] with a PBE functional, to compute the band gap $E_G$, dynamical dielectric tensor $\epsilon_{ij}(\omega)$, and dynamical second-order susceptibility tensor $\chi^{(2)}_{ijk}(\omega)$ of a fully optimized MOF crystal structure with non-centrosymmetric unit cell. All DFT calculations were carried out using the CRYSTAL17 package [39]. The Sellmeier equations
for ordinary and extraordinary crystal axes are obtained from $\epsilon_{ij}(\omega)$, over a frequency range from the near infrared up to the crystal band gap. These are used to establish conditions for perfect phase matching in collinear type-I SPDC [8], with signal output at 1064 nm. The effective nonlinearity $d_{\text{eff}}$ is obtained by contracting the $\chi^{(2)}$ tensor with the appropriate input and output field polarizations. $d_{\text{eff}}$ is used to parametrize an effective Hamiltonian for the SPDC process. The number of entangled photon pairs produced by the MOF, as well as the temporal and spectral properties of the entangled pair wavefunction are computed from the effective Hamiltonian in first order perturbation theory. The $G^{(2)}$ function is fully determined by the photon pair wavefunction and the coincidence detection bandwidth.

### B. Phase matching conditions

The predicted band gaps $E_G$ for the MOFs studied in this work are given in Table I. For comparison, we also compute the band gap of IRMOF-1, with results that agree well with experiments and previous calculations [40–42]. For IRMOF-1, the PBE-GGA functional is found to be in better agreement with experiments than the B3LYP-D calculations used in Ref. [43], which overestimate the band gap. As mentioned above, the PBE-GGA functional is used for MIRO-101, MIRO-102, and MIRO-103. As additional validation of our methods, we also compute the band gaps of $\beta$-barium borate (BBO) and potassium dihydroven phosphate (KDP), two widely used inorganic nonlinear crystals. The results are in good agreement with measured band gaps, although further basis set optimization may be needed for KDP.

In Fig. 2, we show the unit cell structures and the Sellmeier curves $n^2(\lambda)$ of our target MOFs. We obtain these from the dielectric tensor $\epsilon_{ij}(\omega)$, computed at regular wavelength intervals from $\lambda_{\text{min}} = hc/E_G$ to $\lambda_{\text{max}} = 1100$ nm. For the phase-matching geometry considered below, we are interested in the Sellmeier curves along the ordinary axis ($n_o$) and the extraordinary $c$-axis ($n_e$). For each crystal axis, we fit the ab-initio curves to the standard relation

$$n^2(\lambda) = A + \frac{B \lambda^2}{\lambda^2 - C} + \frac{B_1 \lambda^2}{\lambda^2 - C_1}.$$  (1)

The fitted Sellmeier coefficients for each MOF are given in the SM. MIRO-101 is negative uniaxial ($n_e < n_o$), MIRO-103 is positive uniaxial ($n_e > n_o$). Although MIRO-102 is biaxial, one can always fix the crystal orientation such that light propagation is influenced
TABLE I: Calculated [calc] and measured [exp] band gaps $E_G$ for MIRO-101, MIRO-102, and MIRO-103 single crystals. Values for IrMOF-1, β-barium borate (BBO) and potassium dihydrogen phosphate (KDP) are shown for comparison.

|          | $E_G$ (eV) [calc] | $E_G$ (eV) [exp] |
|----------|------------------|------------------|
| MIRO-101 | 3.15             |                 |
| MIRO-102 | 3.10             |                 |
| MIRO-103 | 2.98             |                 |
| IrMOF-1  | 3.62             | 3.4–4.0 [40–42] |
| BBO      | 6.18             | 6.43 [44]       |
| KDP      | 5.90             | 7.12 [45]       |

by two refractive indices only [46]. We aim for obtaining accurate values for the dynamic birefringence $\Delta n(\omega) \equiv n_e(\omega) - n_o(\omega)$ through the frequency range of interest, as this is the observable that most strongly determines the phase matching conditions in SPDC. The phase matching conditions are invariant with respect to an overall change of the static average refractive index $\bar{n} = [n_e(\lambda) + n_o(\lambda)]/2$ for $\lambda \to \infty$. In other words, we can vertically shift all the Sellmeier curves in Fig. 2 by a constant value, and the phase matching results discussed below would not be affected.

SPDC is a three-wave mixing process in which photons from a strong pump laser field at frequency $\omega_p$ are coherently converted into a pair of signal photons with frequencies $\omega_1$ and $\omega_2$ such that $\omega_p = \omega_1 + \omega_2$ [8], as expected for a perturbative light-matter interaction process that conserves energy. In the photon conversion process, conservation of momentum leads to the condition for perfect phase matching $k_p = k_1 + k_2$, where $k$ is a wavevector. In general, phase matching is a vectorial condition that together with energy conservation determines the propagation directions and frequencies of the photons generated in an entangled pair. Several possibilities can be analyzed, depending on the polarizations and propagation directions of interest in experiments [47]. We consider collinear phase matching, in which the pump and signal photons share the same propagation direction $k$. The perfect phase matching condition thus reduces to a scalar relation for the refractive indices given by $\omega_p n_p(\omega_p) = \omega_1 n_1(\omega_1) + \omega_2 n_2(\omega_2)$, where $n_p$ is the refractive index of the pump wave, $n_1$ and $n_2$ are the refractive indices of the signal photons. By further assuming that the signal photons
FIG. 2: MOF structures and ab-initio Sellmeier curves. (a) Unit cell for $\text{Zn}(3-$ptz)$_2$ (MIRO-101), (b) $\text{[Zn(H}_2\text{O)}_6]\text{NO}_3−2(3-$ptz) (MIRO-102), (c) $\text{CdN}_3(3-$ptz)$_2$ (MIRO-103). Color code displays hydrogen atoms (white), carbon (gray), nitrogen (blue) and zinc (violet). The corresponding Sellmeier curves for the extraordinary ($n_e$) and ordinary axes ($n_o$) of each crystal structure, are shown to the right of each structure.

are degenerate ($\omega_1 = \omega_2 = \omega_p/2$), the condition reduces to $n_p(\omega_p) = n_s(\omega_p/2)$, where $n_s(\omega)$ denotes the refractive index of the signal photons. An additional ambiguity remains regarding the polarizations of the pump and signal waves. For the negative uniaxial MIRO-101 and MIRO-103 crystals, we adopt conventional $oee$ type-I conditions [13], where the entangled signal photons are polarized along the ordinary axis ($o$), and the pump is polarized along the extraordinary axis ($e$). For MIRO-102, $eoo$ type-I conditions are used.

In a collinear configuration, the common propagation vector $\mathbf{k}$ of the pump and signal waves has a polar angle $\theta$ relative to the optical $c$-axis and azimuthal angle $\phi$ with respect to the $X$-axis, as show in Fig. 3a. Consider now that the waves propagate along the $X$-axis ($\theta = \phi = \pi/2$). Signal photons thus have extraordinary polarization along $Z$, and the perfect phase matching condition reads $n_o(\omega_p) = n_e(\omega_p/2)$. From the Sellmeier curves in Fig. 2,
FIG. 3: Type-I phase matching for entangled photon pair generation. (a) For a pump field at frequency $\omega$, wavevector $k$ and polarization vector $e_o$ along the ordinary axis, an entangled photon pair is produced via SPDC with an extraordinary polarization $e_e$. In the collinear scenario, all waves propagate at an angle $\theta$ relative to the optical axis of the crystal ($Z$-direction). We set the azimuthal angle to $\phi = \pi/2$. (b) Perfect phase matching angle $\theta_m$ for MIRO-101, MIRO 102, and MIRO-103 for a range of signal wavelengths. We see that this condition cannot be satisfied for any choice of $\omega_p$ in the visible spectrum. This is common for materials with large birefringence [13]. Perfect phase matching in our uniaxial MOF crystals can still be achieved if the pump and signal waves have propagation components along both ordinary and extraordinary directions. In Fig. 3b, we plot the predicted angle of perfect phase matching $\theta_m$ for MIRO-101, MIRO-102, and MIRO-103, over a range of entangled photon wavelengths $\lambda_s$ in the near infrared. We set $\phi = \pi/2$ here for concreteness, but below this constraint is relaxed when we discuss effective nonlinearities.

C. Entangled photon pair properties

In Fig. 4, we illustrate collinear type-I spontaneous parametric down-conversion (SPDC) in a nonlinear MOF crystal, for the generation of entangled photon pairs in the near infrared. Pump photons from a strong visible laser field are coherently converted into a photon pairs described by a wavefunction of the form

$$|\Psi_2\rangle = \lambda L \int dk_1 \int dk_2 Q(k_1, k_2) \hat{a}^\dagger_{k_1} \hat{a}^\dagger_{k_2} |0\rangle_1 |0\rangle_2,$$  

(2)
FIG. 4: Entangled photon pair generation with metal-organic frameworks. (a) Visible photons (green circles) are pumped into a non-centrosymetric MOF single crystal with propagation length $L$. Entangled photon pairs at half the pump frequency (red circles), emerge from the crystal with a small delay $\tau$. Each pair is collected with a coincidence detector (CD), and the delay times are post-processed to give a two-time correlation function $G^{(2)}(\tau)$. (b) Log-log plot of the correlation time $T_c$ (FWHM) as a function of detector bandwidth $\sigma$ for collinear SPDC with type-I phase matching. Time is in units of $\tau_L = \sqrt{\beta_2 L/4}$. Representative $G^{(2)}$ functions in the narrowband and broadband regimes are shown for comparison. $\beta_2$ is the group velocity dispersion at the pair frequency.

where $L$ is the crystal propagation and $\lambda$ is an effective nonlinear coupling given by

$$\lambda = i \frac{2A_0d_{\text{eff}}}{\hbar} \int d^2r_\perp A_p^*(r_\perp)A_1(r_\perp)A_2(r_\perp), \quad (3)$$

where $A_0$ is the peak field amplitude of the pump laser field, $d_{\text{eff}} = (\epsilon_0/2)\chi^{(2)}_{ijk}\epsilon_i\epsilon_j\epsilon_k$ is the effective second-order nonlinearity obtained as a contraction of the $\chi^{(2)}$ tensor of the crystal and the field polarizations assumed in our phase matching configuration [13]. The spatial integral is the transverse mode overlap between the pump and signal fields. This quantity
depends on the pump beam geometry and the crystal dimensions.

The photon pair (biphoton) wavefunction in Eq. (2) is a non-separable wavepacket of the one-photon frequency-domain contributions $\hat{a}_{k_j}^\dagger |0\rangle_j$, for $j = 1, 2$. The spectral and temporal properties of the biphoton state are determined by the joint spectral function

$$Q(k_1, k_2) = l(\omega_1) l(\omega_2) \text{sinc}(\Delta k L/2) \ e^{i\Delta k L/2} \alpha_p(\omega_1 + \omega_2),$$

(4)

where $\Delta k \equiv k_p - k_1 - k_2$ is the phase mismatch, $\alpha_p(\omega)$ is the normalized pump spectral amplitude evaluated at $\omega_p$, and $l(\omega_j)$ are slowly-varying functions in frequency. Generalizations of Eq. (4) to account for linear losses are straightforward [48]. The derivation of Eq. (2) closely follows Ref. [8], and is reproduced in the Supplementary Material.

The arrival times for all the photon pairs emitted by the MOF crystal are detected in a coincidence setup, as illustrated in Fig. 4a. The probability of detecting a photon at time $t_1$ and a second photon at time $t_2$ is given by the intensity correlation function $G^{(2)}(t_1, t_2) = |\langle 0 | \hat{E}^{(+)}(t_2) \hat{E}^{(+)}(t_1) | \Psi_2 \rangle|^2$ [49], where the far-field operators $\hat{E}^{(+)}(t_j) = \int d\omega f(\omega) \hat{a}(\omega) e^{i\omega t_j}$ take into account any spectral filtering done at the detectors through the filter function $f(\omega)$. For SPDC sources, the $G^{(2)}$ depends only on the relative time $\tau = t_1 - t_2$ [8]. The total coincidence count, i.e., the number of photon pairs detected $N_2$, is proportional to the integral of $G^{(2)}(\tau)$ over all possible delays. According to Eq. (2), $N_2$ scales as $d_{\text{eff}}^2$, which is an intrinsic property of the MOF crystal and band structure that we can evaluate from first principles.

The number of emitted photon pairs produced in SPDC is one of the features that can be attributed to MOF crystals. Another feature that is important in applications is the pair correlation time $T_c$, which is a measure of how indistinguishable (i.e., entangled) are two photons in a pair. $T_c$ can be defined as the width of the $G^{(2)}$ function. Pairs of distinguishable uncorrelated photons cannot be used in entanglement-based applications [16]. In contrast to the number of photon pairs, $T_c$ not only depends on the intrinsic properties of the a given MOF structure, but also on the detection setup. We can specify this dependence by writing an explicit expression for the shape of the $G^{(2)}$. For degenerate type-I phase matching, we have

$$G^{(2)}(\tau) \propto \left| \int d\nu \ \text{sinc} \left[ (\beta_2 L/4) \nu^2 \right] e^{-\nu^2/\sigma^2} e^{i\nu \tau} \right|^2,$$

(5)

where $\beta_2$ is the group velocity dispersion (GVD) of the degenerate signal photons and $\sigma$ is the width of the spectral filter function $f(\omega)$, assumed Gaussian for simplicity. The integration
TABLE II: Calculated phase matching angle $\theta_m$, $d_{\text{eff}}$ evaluated at the propagation direction ($\theta_m, \phi$) in collinear type-I SPDC at 1064 nm, group velocity dispersion (GVD) at perfect phase matching for ordinary ($o$) and extraordinary ($e$) propagation directions, and the corresponding photon pair correlation times $T_c$. Our calculated $\theta_m$ and $d_{\text{eff}}$ for BBO and KDP are compared with experimental values from Ref. [50]. In all cases we set the crystal length to $L = 1.5$ mm.

| MOF     | $\theta_m$ | $d_{\text{eff}}$ | $\phi$ | $\text{GVD}_o$ | $\text{GVD}_e$ | $T_c^o$ | $T_c^e$ |
|---------|------------|------------------|--------|----------------|----------------|---------|---------|
| MIRO-101| 20.8       | −0.35            | 80º    | 213.18         | 77.60          | 17.88   | 10.78   |
|         |            | +0.35            | 170º   |                |                |         |         |
| MIRO-102| 26.1       | +0.08            | 90º    | 204.47         | 114.12         | 17.51   | 13.08   |
| MIRO-103| 25.4       | +0.12            | 0º     | 129.92         | 243.18         | 13.96   | 19.1    |
| BBO (calc) | 22.9   | 1.82             | 0º     | 38.01          | 37.11          | 7.55    | 7.46    |
| BBO (exp) | 22.8 [50] | 2.11 [50]        |        |                |                |         |         |
| KDP (calc) | 40.4   | 0.41             | 45º    | −8.04          | 19.83          | −       | 5.46    |
| KDP (exp) | 41 [50]  | 0.29 [50]        |        |                |                |         |         |

over the frequency detuning $\nu$ accounts for all possible signal photons that do not satisfy perfect phase matching conditions $\Delta k = 0$, but still satisfy energy conservation. We neglect deviations from $\Delta k = 0$ beyond second order in $\nu$. Photons in a pair with detuning much larger than the detector bandwidth do not contribute to the correlation function, even if they arrive at the same time ($\tau = 0$) at the detectors.

In Fig. 4, we plot the correlation time $T_c$ for type-I SPDC under collinear type-I phase matching as a function of the detector bandwidth $\sigma$ (log-log scale). Time is in units of the characteristic crystal timescale $\tau_L = \sqrt{\beta_2 L/4}$, which roughly corresponds to the width of the sinc function in Eq. (5). In the broadband detection limit ($\sigma \gg 1/\tau_L$), we have that $T_c \approx 2.0 \tau_L$. Therefore, given a crystal length $L$, we can compute $T_c$ for a given MOF crystal by evaluating $\beta_2$ from the Sellmeier curve obtained from first principles. For concreteness, the GVD parameter for MIRO-101 under conditions of perfect phase matching at $\lambda = 1064$ nm is estimated to be $\beta_2 = 77.60$ fs$^2$/mm. For a crystal length $L = 1.5$ mm, the estimated correlation time is $T_c \approx 10.78$ fs for this MOF crystal. Figure 4 shows that this broadband...
value only represents a lower bound for $T_c$ for this crystal, since the biphoton wavepacket is expected to broaden in time when a finite detector bandwidth is taken into account. For example, by using a spectral filters with a relatively broad linewidth $\sigma = 0.2/\tau_L \approx 15$ THz (FWHM), the coincidence correlation time now becomes $T_c \approx 155$ fs, for the same crystal parameters.

In Table II, we summarize the results obtained for SPDC with collinear type-I phase matching for MIRO-101, MIRO-102, and MIRO-103 crystal slabs with length $L = 1.5$ mm. We obtain angles of perfect phase matching $\theta_m$ at 1064 nm, the effective nonlinearity $d_{\text{eff}}$ at perfect phase matching, and the characteristic crystal timescales $\tau_L$ for ordinary and extraordinary signal field polarizations. For a given coincidence detection bandwidth $\sigma$, the photon pair correlation time $T_c$ can be readily estimated. As an additional validation of our DFT methods, we also compared our obtained parameters for the inorganic crystals BBO and KDP, obtaining results that agree well with experiments [50].

III. CONCLUSIONS

In this work, we develop multi-scale methodology for the computational characterization of quantum light generated by nonlinear metal-organic frameworks. Specifically, we study entangled photon pair generation in the near infrared via spontaneous parametric down conversion (SPDC) in three zinc-tetrazole MOF crystals with non-centrosymmetric unit cell: $\text{Zn}(3-\text{ptz})_2$ (MIRO-101), $\text{[Zn(H}_2\text{O)}_6]\text{NO}_3\text{2(3-}\text{ptz})$ (MIRO-102) and $\text{CdN}_3\text{(3-}\text{ptz})_2$ (MIRO-103). Using solid-state DFT, we determine the band gaps and Sellmeier equations of these crystals. The MOFs studied are strongly birefringent, and allow conditions for type-I and type-II phase matching in SPDC. We focus on a collinear type-I scenario to illustrate the potential of our method for understanding the temporal and frequency correlations of the entangled photon pair (biphoton) wavefunction produced under strong laser pumping of the MOF crystals studied. Other phase matching scenarios are straightforward extensions of our type-I results. Our work thus paves the way for the computational discovery of novel metal-organic framework materials that are favorable for target applications in optical quantum technology.
IV. CONFLICTS OF INTEREST

There are no conflicts to declare.

V. ACKNOWLEDGEMENTS

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