

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

- Title: Giant Enhancement of Second Harmonic Generation Accompanied by the Structural Transformation of 7-fold to 8-fold Interpenetrated MOF
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201911632 Angew. Chem. 10.1002/ange.201911632

Link to VoR: http://dx.doi.org/10.1002/anie.201911632 http://dx.doi.org/10.1002/ange.201911632

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Giant Enhancement of Second Harmonic Generation Accompanied by the Structural Transformation of 7-fold to 8-fold Interpenetrated MOF

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Dedicated to Prof K.C. Patil

Abstract: Interpenetration in metal-organic frameworks (MOFs) is an intriguing phenomenon with significant impacts on the properties, and functional applications of MOFs. Herein, we showed that a 7-fold interpenetrated MOF is transformed to an 8-fold interpenetrated MOF by the loss of DMF in a single-crystal-to-single-crystal manner. This is accompanied by a giant enhancement of the second harmonic generation (SHG ~125 times) and two-photon photoluminescence (~14 times). The strengthened π - π interaction between the individual diamondoid networks and intensified oscillator strength of the molecules render the augment of dipole moments and boost the nonlinear optical conversion efficiency. Large positive and negative thermal expansions of 1 occur at 30-150°C before the loss of DMF. These results offer an avenue to manipulate the NLO properties of MOFs using interpenetration and provide access to tunable single-crystal NLO devices.

Introduction

Metal-organic Framework (MOF) structures are generally known to be very robust upon removal of solvents from the channels^{1,2} and they are responsible for various applications.3-10 Interpenetration is a well-known and ubiquitous phenomenon in MOFs^{10–15} wherein the degree of interpenetration has been varied from two to twelve, and rarely to as high as 54.16 For any given chemical composition, the degree of interpenetration can be manipulated by experimental conditions.¹⁷⁻²² Since there are no bonds between the interpenetrated structures, it was thought difficult to manipulate the degree of interpenetration of MOFs in the solid state. However, the dynamic structural transformation between different orders of interpenetration upon removal of the coordinating solvents or solvents in the channels has been successfully achieved by Chen, Kim, and Barbour.23-27 Interestingly, some of these conversions were found to occur in a single-crystal-to-single-crystal fashion (SCSC).23-26

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Second-order nonlinear optical (NLO) properties present in the non-centrosymmetric solids have widespread applications in the emerging field of photonics for optical signal transmission and processing.²⁸⁻³⁰ Non-centrosymmetric MOFs can be rationally designed and constructed from carefully chosen rigid bridging ligands with the desired metal coordination geometries. For this purpose, diamondoid network (dia net) is the most suitable choice as the four-connected nodes and unsymmetrical bridging ligands as they lack inversion centers. This has been amply demonstrated by Lin and co-workers.³¹⁻³³ It should be noted that the chiral ligands may ensure the MOFs to be NLO active, but they do not necessarily display strong second harmonic generation (SHG) responses as the dipoles of chromophoric building blocks do not have to orient in a noncentrosymmetric fashion. Hence a direct correlation between the observed SHG response and the structures is not fully established.31,34

Results and Discussion

During the syntheses of Zn(II) MOFs using trans-2-(4-pyridyl)-4vinylbenzoate (pvb) ligand under different experimental conditions, we isolated two MOFs with dia topology namely, [Zn(pvb)₂]·DMF (1) and [Zn(pvb)₂] (2) and they have 7-fold and 8fold interpenetrations, respectively. Interestingly, both 1 and 2 crystallized in non-centrosymmetric space group Cc^{35,36} and C2 respectively.37,38 The Zn(II) atoms in 1 have a distorted fivecoordinate geometry via bonding to two pyridyl N atoms, two O atoms of a chelating carboxylate group and an O atom from a monodentate carboxylate group. The $Zn(I) \cdots O(4)$ distance, 2.837 Å which is close to the sum of the van der Waal's radii of 2.91 Å, is not considered here as a bond. The Zn(II) node extends the structure into a dia framework (Figure 1a) with 7-fold interpenetration (Figure 1b and Figure S1). The individual nets are related by translational symmetry of 8.39 Å corresponding to the crystallographic c-axis. A solvent accessible void volume of 23.4% in 1 was partially occupied by a DMF molecule.35,36





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Compound **2** crystallized from a solvent mixture of DMA and water, has no guest solvent retained in the lattice. The two crystallographically distinct Zn(II) atoms lie on the 2-fold axes coordinating to two carboxylate groups and two pyridyl ligands. Zn1 has a distorted octahedral coordination environment with two chelating carboxylates and two pyridyl *N* atoms, whereas Zn2 has a tetrahedral geometry with both coordinating carboxylates in monodentate mode (Figure 2a). This **dia** net packs tightly into an 8-fold interpenetrated network with no solvent accessible void (Figure 2b and Figure S2). The interpenetration translates along the crystallographic *b*-axis.^{37, 38} The adamantoid cage was found to exist with an edge length of 15.31 Å, an apical distance of 26.11 Å, 21.88 Å and 27.78 Å, with a diagonal Zn····Zn length of 43.20 Å along the *c*-axis.



Figure 2. (a) A view showing the dia net in 2. Legends: Zn – green, O – red, N – blue and C – gray. (b) the 8-fold interpenetrated nets in 2.

The thermogravimetry (TG) analysis shows that the DMF guest in **1** starts losing very slowly from room temperature and then rapidly in the temperature range, 110-210°C. The experimental weight loss of 12.7% indicates the loss of a DMF (calculated: 12.5%) (Figure S5). Interestingly the X-ray powder diffraction (XRPD) pattern of the desolvated **1** is similar to that of **2** as shown in Figure 3. This observation shows that the 7-fold interpenetrated **dia** MOF, **1** has been transformed to 8-fold interpenetrated **2** by the removal of DMF. This transformation from **1** to **2** has also been shown to occur in an SCSC manner. Switching of the degree of interpenetration in MOFs by external stimuli have been rarely observed in the literature.^{24–28}

The Cu(II) MOF, $[Cu(pvb)_2]$ -DMF, **3** synthesized similar to **1**, is also isomorphous and isostructural to **1** (Figure S3). The TG shows the loss of DMF (Found: 12.8% and Calculated: 12.5%) in the temperature range 30-190°C (Figure S7). The VT- XRPD patterns reveal that the removal of DMF from **3** does not influence any structural change like **1** (Figure S15 and Figure S16 in SI). The non-centrosymmetric group *Cc* was still maintained in the crystal after cooling to room temperature. This occurs in an SCSC fashion with small reduction in cell volume from 2743.0(2) Å³ to 2670.1(2) Å³ from the single crystal X-ray diffraction (SC-XRD) data at -100°C. After DMF removal, the crystal absorbed moisture from air to form [Cu(pvb)₂]-2H₂O (**4**) (Figure S8).

Variable temperature XRPD (VT-XRPD) studies of **1** from 30°C to 190°C were performed under vacuum condition using a a capillary microreactor (Figure S9 in SI) to remove guest DMF in the lattice. The *in-situ* XRPD measurements reveal that the transition from *Cc* phase to *C*2 phase starts at *ca*. 110°C and



Figure 3. XRPD patterns of (a) 1 simulated from the crystal structure at 100 K, (b) as-synthesized crystal 1 at RT, (c) 2 crystals at 30° C under vacuum condition, (d) 2 simulated from the crystal structure at 100 K.

almost completes at 160°C with no other intermediate phases (Figure S10-12 in SI). In contrast to the β angle of 94.2° from the SC-XRD data for **2** at -100°C, the high-temperature *C*2 phase shows β angle close to 90° which is retained at 30°C.



Figure 4. VT-XRPD patterns showing the conversion of 1 (red) to 2 (blue) during desolvation process under vacuum condition.

The structural transformation from **1** to **2** is accompanied by decrease in the cell volume of 312.4 Å³ and decrease in the density from 1.396 g/cm⁻³ to 1.376 g/cm⁻³. Interestingly, **3** has a structure similar to **1**, but it behaves differently. A plausible mechanism for the structural transformation of **1** to **2** and the behavior of **3** may be envisaged as follows. When the DMF guest molecules in **1** were removed from the 1D channels along *c*-axis by heating, alternating **dia** fragments from the adjacent structures move towards each other to fill the voids. Due to these movements, the Zn(II)-ligand bonds are broken and reformed. In this process, the interpenetration increased, the length of the *b*-axis in **1** is drastically reduced from 24.964 Å to 21.603 Å which becomes *a*-axis in **2**. The original *c*-axis in **1** becomes *b*-axis in **2** with *C*2 space group. This has been accompanied by drastic

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changes of the distorted trigonal bipyramidal geometry of Zn(II) in 1 to a mixture of octahedral and tetrahedral geometries in 2.

The thermal behavior of **1** was further investigated using the data from VT-XRPD measurements under vacuum condition in the temperature range 30-140°C. Sequential Rietveld refinements were performed to determine the unit cell parameters as a function of temperature. The coefficients of thermal expansion were calculated using the program PASCal (Table 1).³⁹ The crystal **1** exhibits strong anisotropic thermal expansion with high positive thermal expansion (PTE) along the principal X₃-axis (α_3 = 225.0249 x 10⁻⁶ K⁻¹, parallel to the crystallographic *b*-axis), relatively small PTE along the principal X₂-axis (α_2 = 88.8589 x 10⁻⁶ K⁻¹, nearly parallel to the crystallographic *c*-axis) and high negative thermal expansion (NTE) along the principal X₁-axis (α_1 = -199.5967 x 10⁻⁶ K⁻¹, almost parallel to the direction [2 0 1] with the *a*-axis as the most influent component axis). All expansions are rather linear in the measured temperature range (Figure S21).

 Table 1. Volume expansion coefficients and all axes expansion coefficients for 1 using the program PASCal^a.

Axes	α, 10 ⁻⁶ K ⁻¹	σ _α 10 ⁻⁶ K ⁻¹	а	Direction b	С
X ₁	-199.5967	24.5302	-0.8393	0.0000	-0.5436
X2	88.8589	16.7810	-0.1614	-0.0000	0.9869
X ₃	225.0249	4.4317	0.0000	-1.0000	0.0000
V	111.9961	4.8511			

^a α_1 is the linear coefficient of thermal expansion, σ_α is the error in the linear coefficient of thermal expansion, *a*, *b*, and *c* are the projections of X_n on the unit cell axes.

Table 1 shows interesting anisotropic thermal expansion for 1. The base of the dia net can be approximated to a rectangle containing six atoms of Zn(II) (Figure 5 and Figure S22 in SI). The long side includes two ligands that bridge three Zn(II) atoms and it runs along the $[2 \ 0 \ \overline{1}]$ direction. The short side includes one ligand that bridges two Zn(II) atoms and it runs along $\begin{bmatrix} 1 & 1 & \overline{2} \end{bmatrix}$ direction. An expansion along both directions is inhibited since it stretches the ligands. However, the two bridged ligands along the long side do not form a rigid unit but may bend due to the change of the angles formed by the Zn(II) nodes (black double arrows) leading to a distortion of the rectangular motif along b- and c- axes (principal X₃- and X₂- axis, respectively). Moreover, since the framework is packed along c- axis which is parallel to the direction of the channels filled with DMF molecules, the movement of the molecules along the direction of the channels (c- axis) is hindered whereas towards the channels (ab plane) is promoted. Therefore, the preferred direction of the expansion is along b axis. As a consequence of the bending and the subsequent distortion of the rectangular motif, compression along the principal X1-axis is promoted by mechanics.

The large positive and negative thermal expansion coefficient values observed in **1** are interesting and significant. Most of the MOFs show either large positive⁴⁰⁻⁴² values or negative⁴³⁻⁴⁸

values. It is not common for solids to show large positive and negative thermal expansion (Table S2).^{49–51}



Figure 5. Representation of the rectangular motif of **dia** net in **1** along (a) *a* axis, (b) *b* axis and (c) *c* axis. The principal axes $(X_1, X_2 \text{ and } X_3)$ for thermal expansion are also given. The long side is indicated by the light blue line, the short side in purple and the angle formed by Zn(II) nodes by black double arrows

Micrometer-scale crystals of 1 and 2 were ground and dispersed in DMF solution for linear optical characterization. Both of 1 and 2 exhibited dominant absorption band with a maximum at ~317 nm owing to the absorption of Hpvb ligand and a new absorption band at 380 nm with long tails extending to the visible range (Figure 6a, solid line). The Zn(II) ions do not contribute to the absorption in the visible region because it has a closed shell (d¹⁰). This new absorption band might be due to the metal-ligand interactions. The emission of **1** (λ_{max} = 460 nm, τ_1 = 2.33 ns, Φ_1 = 1.1%) can be probably assigned to intra-ligand fluorescent emission since a similar emission peaked at 460 nm observed for Hpvb ligand (Figure 6). 52 The emission peak of $\boldsymbol{2}$ (λ_{max} = 478 nm, τ_2 = 0.90 ns, $\Phi_2 = 5.4\%$) displayed a redshift of 18 nm compared to **1** (Figure 6). Owing to the absence of DMF molecules, the individual dia nets of **2** are closer to each other with increased $\pi - \pi$ interactions, resulting in redshifted emission.53 The radiative decay rates of 1 and **2** ($k_r^1 = 0.0047 \text{ ns}^{-1}$, $k_r^2 = 0.06 \text{ ns}^{-1}$) were determined from the measured lifetime (τ) and quantum yield (Φ): $k_r = \Phi/\tau$. Based on theoretical Strickler–Berg equation: $k_r = 0.668 \langle \tilde{v} \rangle_{av}^2 n^2 f$, the radiative decay rate is proportional to the oscillator strength of the pertinent electronic transition.⁵⁴ The results indicated an increase in magnitude of the oscillator strength and transition dipole moment in 2 compared to 1.



Figure 6. (a) Absorption and PL ($\lambda_{EX} = 340$ nm) spectra of compound **1**, **2** and Hpvb ligand. (b) Time-resolved emission spectroscopy of compound **1**, **2** and Hpvb ligand with 340 nm excitation. The time-resolved photoluminescence (TRPL) curves of **1** and ligand were fit with single-exponential decay, which possessed a lifetime about $\tau_1 = 2.33$ ns and $\tau_L = 1.05$ ns, respectively. While TRPL of **2** was fit with bi-exponential decay with an average lifetime around $\tau_2 = 0.90$ ns ($A_{21} = 0.73$, $\tau_{21} = 0.25$ ns; $A_{22} = 0.27$, $\tau_{22} = 2.66$ ns). 2PPL (c, $\lambda_{EX} = 680$

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nm) and SHG (d, λ_{EX} = 950 nm) spectra of the single crystals of 1 and 2. Excitation power is 1mW.

Nonlinear optical responses of **1** and **2** were characterized by mapping SHG (λ_{EX} = 950 nm) and 2PPL (λ_{EX} = 680 nm) responses of the single crystals. The experimental setup was shown in Figure S23. The sample was placed on a quartz substrate on a piezo-stage. The bright field optical images of crystals of **1** and **2** are shown in Figure S24a-b. Spatial distribution of SHG and 2PPL intensities of crystals of **1** and **2** in the zoomed area is shown in Figure S24c-f. Crystal of sample **2** displays strong SHG response throughout the bulk area. In contrast, the crystal **1** displayed weak SHG response in the bulk area except for strong SHG response at the boundary area and interface between the single crystals due to the edge effect.^{55,56} 2PPL response of the crystal of sample **2** in the bulk area is much stronger than that of sample **1**.

SHG and 2PPL responses of single crystals were further investigated by focusing the laser beam at a specific non-edged area of the single crystals (see red dots or circles in Figure S24af) to avoid the edge effect. The excitation wavelength was varied from 680 to 1100 nm. Zn(II) MOFs (1 and 2) display broadband 2PPL signals in the wavelength range of 400-600 nm (Figure 6c). The excitation power dependence of the multi-photon PL and SHG signals displayed quadratic power dependence, validating 2PPL and SHG (Figure S25). SHG signals of both 1 and 2 were strongly excitation wavelength dependent, with optimum SHG responses at 475 nm, coincident with their fluorescence maximum (Figure S26a-b). This kind of phenomenon has been previously rationalized by a 'two-state' model.⁵⁷ According to this model, frequency doubling will be enhanced when the SHG signal approaches to the frequency of the lowest optical transition.⁵⁷ At the optimum excitation wavelength of 950 nm, the SHG response at 475 nm from the crystal 2 is ~125 times larger than that of 1 (Figure 6d). 2PPL of both samples 1 and 2 display the strongest 2PPL responses at 680 nm, the shortest wavelength in the wavelength range from 680 to 800 nm (Figure S26c). Under this optimum excitation wavelength, the 2PPL intensity of sample 2 is ~14 times stronger than that of sample 1 (Figure 6c).

Moreover, we synthesized $[Cu(pvb)_2]$ -DMF, **3** which is isotypical to **1**, for comparison. The VT- PXRD patterns revealed that removal of DMF from **3** does not result in structural change as **1** (Figure S15 and Figure S16). The non-centrosymmetric group *Cc* remined in the DMF removed solid, $[Cu(pvb)_2]$ -2H₂O, **4** after cooling to the room temperature. The absorption spectrum of **3** and **4** are shown in Figure S27. Both **3** and **4** were found to display optimum SHG responses at 900 nm. Under excitation at 900 nm, SHG responses of the solvated and desolvated **3** and **4** are comparable to each other (Figure S28), which is strikingly different from the behaviors of **1** and **2**. These results suggest that structure transformation accompanied by 7-fold to 8-fold interpenetration in Zn(II) MOFs is responses of the solvated and desolvated structures.

Generally, the nonlinear optical responses are determined by the overall magnitude of the dipole moment in the crystals.⁵⁸⁻⁶⁰ Along with the 7-fold to 8-fold interpenetration change, the loss of

DMF brings the individual **dia** nets closer to each other which facilitates the interactions between them. The π - π interactions between individual **dia** nets were strengthened as revealed by the red-shifted emission spectrum of **2** (Figure 6a green dot line). The strengthened π - π interaction consequently caused increased oscillator strength of **2**, which is proportional to the square of transition dipole moment. Under the external electric field, the electrons are delocalized and can easily move, which ultimately lead to an increase in total dipole moment and the asymmetry of the system.⁶¹ The results show that increased interpenetration induces larger transition dipole moment of **2**. These could cause larger 2PPL and SHG responses of **2** compared with its solvated form **1**.

To determine the effective second-order nonlinearity, |deff|, SHG signals from a urea crystal were measured by using the same experimental setup for direct comparison. Urea is one of the commercially-available single crystals that possess large secondorder nonlinearity (~1 pm/V). The absolute |deff| value of MOFs single crystals was determined by using urea as the reference. Two-photon absorption cross-sections (Figure S26c) of the samples were also obtained by comparison with perylene powder (detailed calculations see Supplementary Methods). Table 2 summarizes the second-order nonlinearity (|deffi) and two-photon absorption cross-sections (σ_2) of the Zn(II) and Cu(II) MOFs. The |d_{eff}| of 2 is determined to be 14.4 pm/V which is 10 times upsurge compared with 1. However, this is not the highest activity reported as compared to the literature.31-33,62 In contrast, second-order nonlinearity of the Cu(II) MOFs is comparable to that of the desolvated solid 4 compared to solvated 3 as they do not experience interpenetration change. Two-photon absorption cross-section of sample 2 is about 3 times that of sample 1.

Table 2. Summary of second-order nonlinearity ($|d_{eff}|$ at 950 nm for 1 and 2, 900 nm for 3 and 4) and two-photon absorption cross-sections (σ_2 at 680 nm) of Zn(II), Cu(II) MOFs.

Sample	1	2	3	4
Second-order nonlinearity d _{eff} (pm·V ⁻¹)	1.3	14.4	4.0	5.4
Two-photon absorption cross-section σ_2 (10 ⁻² GM)	12	37	NA	NA

Conclusion

Change in the interpenetration of MOFs by the removal of guest molecules in the channels is an interesting phenomenon. Only a very few examples have been reported in the literature. Large positive and negative thermal expansions of **1** has been observed in the temperature range 30-150°C before the loss of DMF and transformation to **2**. The coordination linkages are sufficiently labile even in the solid state to allow the change in interpenetration to proceed in an SCSC manner. A deeper understanding of this dynamic structural transformation would be beneficial to gain better control of their properties. Increase in interpenetration not only reduces porosity but also increase inter-lumophore interactions.⁶³ Here we observed that the solid-state

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structural transformation between two non-centrosymmetric Zn(II) MOFs enhanced the SHG signal very significantly (~125 times). The absolute $|d_{eff}|$ value of single crystals increased from 1.3 (for 1) to 14.4 pm·V⁻¹(for 2). The loss of the DMF molecules resulted in stronger interactions between individual **dia** nets and enhanced π – π interactions. On the other hand, the oscillator strength increased. Both effects caused an increased magnitude of the transition dipole moment, and consequently boosted SHG efficiency of 2. Our work provides new insight into how the NLO properties can be tuned by the variation of the interpenetrations to improve the optical properties of the Zn(II) MOFs for NLO devices for specific functions such as NLO quantum computing devices and highly monochromatic lasers.

Acknowledgements

JJV thanks the Ministry of Education Singapore for the Tier 1 grant (WBS R-143-000-A12-114 and R-143-000-B13-114). Frank Adams from MPI Stuttgart is acknowledged for use of the capillary micro-reactor. GG thanks Prof. Consiglia Tedesco, University of Salerno, Italy for granting permission to do his PhD research under Prof Robert E. Dinnebier at MPI Stuttgart. VAS, Department of Technology, Shivaji University, Kolhapur, Vidyanagar, Kolhapur 416004, India is thankful to SERB, DST, Government of India for Overseas Postdoctoral Fellowship to work with JJV at NUS. AC is currently working at the Department of Science, M.A. College of Engineering, Kothamangalam - 686666, Kerala, India.

Keywords: Metal-organic frameworks • Interpenetration • Nonlinear optics • Second harmonic generation • Single-crystalto-single-crystal manner

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A 7-fold to an 8-fold transformation of MOFs by the loss of DMF is accompanied by a giant enhancement of the SHG and two-photon emission facilitated by the increased π - π interaction and oscillator strength. This demonstrates a way to manipulate the NLO properties of MOFs using interpenetration for tunable single-crystal NLO devices.

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Zhihui Chen, Gianpiero Gallo, Vaishali A. Sawant, Tianxiang Zhang, Menglong Zhu, Liangliang Liang, Anjana Chanthapally, Geetha Bolla, Hong Sheng Quah, Xiaogang Liu, Kian Ping Loh, Robert E. Dinnebier*, Qing-Hua Xu *, and Jagadese J Vittal*

Giant Enhancement of Second Harmonic Generation Accompanied by the Structural Transformation of 7fold to 8-fold Interpenetrated MOF

