Electronic Supplementary Information (ESI)

Impressive Second Harmonic Generation Response in a Novel Phase-Matchable NLO-active MOF Derived from Achiral Precursors

Yu-Xiao Zhang,^{a,b} Bing-Xuan Li,^a Hua Lin,^{*,a} Zuju Ma,^{*,c} Xin-Tao Wu^a and Qi-Long

Zhu^{*,a}

^aState Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China ^bUniversity of Chinese Academy of Sciences, Beijing 100049, China ^cSchool of Materials Science and Engineering, Anhui University of Technology, Maanshan 243002, China E-mail: linhua@fjirsm.ac.cn; zjma@outlook.com; qlzhu@fjirsm.ac.cn

1 Experimental Section

1.1 Materials and Instruments

3,5-bis(4'-carboxyphenyl)-1,2,4-triazole (H₂bct), Zn(NO₃)₂·6H₂O, methanol (MeOH) and N,N'-dimethylformamide (DMF) were purchased from commercial sources and used as received without further purification. Luminescence spectra were acquired on a Hitachi F-7000 FL spectrophotometer. Elemental analysis for C, H and N was performed with an Elementar Vario MICRO CHNOS elemental analyzer. Infrared (IR) spectrum was obtained through a PerkinElmer Spectrum One FT-IR spectrometer together with KBr pellets from 4000 to 400 cm⁻¹. Thermogravimetric (TG) analysis was carried out using a NETZSCH STA449C equipment from 30 to 900 °C with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. UV-vis diffuse reflectance spectrum was measured on a PerkinElmer LAMBDA 950 UV/Vis/NIR Spectrophotometer with BaSO₄ as the reference and ranging from 600 to 250 nm. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Desktop Mini Flex-II diffractometer using Cu K α radiation ($\lambda = 1.54056$ Å) at 30 kV and 15 mA with 20 (5–50°).

1.2 Synthesis

Single crystals of **MOF-FJ1** were prepared through a solvothermal method. A mixture of H₂bct (30.9 mg, 0.1 mmol) and Zn(NO₃)₂·6H₂O (29.8 mg, 0.1 mmol) in H₂O/DMF/MeOH (8 mL, v/v/v, 1:1:2) was placed into a Teflon-lined autoclave, heated at 100 °C for 2 days and then cooled to room temperature for another 1 day. Colorless platy crystals suitable for single-crystal X-ray diffraction (SCXRD) and NLO measurement were isolated by filtration and then washed with DMF for several times. Yield: ca. 70% based on H₂bct. Anal. Calcd (%) for ZnC₁₆H₁₃N₃O₆: C 47.02, H 3.21, N 10.28. Found: C 44.70, H 3.20, N 9.51. IR (KBr, cm⁻¹): 3170(m, broad), 1594(s), 1566(s), 1545(s), 1524(m), 1414(s), 1372(s), 1289(m), 1191(m), 1131(m), 996(m), 862(s), 787(m), 742(s), 698(m), 580(w), 556(m), 492(w), 437(w).

1.3 Single-Crystal X-ray Diffraction (SCXRD) Studies

The crystallographic data of **MOF-FJ1** were collected on a Rigaku Saturn 724HG CCD diffractometer using Mo-K_a radiation ($\lambda = 0.71073$ Å graphite-monochromator) at room temperature. Using *SHELXTL-2017* program package and *OLEX2* program¹, the structure was solved by *ShelXS* program² using directed method and refined by ShelXL program² using full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated geometrically. *PLATON* software³ was used to analyze π - π interactions. Ultimately, the molecule formula of **MOF-FJ1** was calculated from the SCXRD data together with the results of TG and elemental analysis.

1.4 Characterization of MOF-FJ1

The TG curve of **MOF-FJ1** shows that the first mass loss of 8.85% below 220 °C can be attributed to the release of 2 coordinated water molecules (calcd 8.82%), while the weight loss above 400 °C suggests the decomposition of the organic ligands. The well matching between PXRD pattern obtained from as-synthesized sample and simulated one confirms the purity and homogeneity of the as-synthesized sample of **MOF-FJ1**.

2 Computational details

The DFT calculations have been performed using the *Vienna ab initio simulation package* (VASP)^{4–6} with the Perdew-Burke-Ernzerhof (PBE)⁷ exchange correlation functional. The projected augmented wave (PAW)⁸ potentials with the valence states 2s and 2p for C, N and S, 1s for H, 3d and 4s for Zn, respectively, have been used. A Γ -centered 5×3×1 Monkhorst-Pack grid for the Brillouin zone sampling⁹ and a cutoff energy of 500 eV for the plane wave expansion were found to get convergent lattice parameters. Both the cell and atomic relaxations were carried out until the residual forces are below 0.02 eV Å⁻¹. A Monkhorst-Pack k-point mesh⁶ of 7×3×1 was used for the calculation of the linear and nonlinear optical properties.

The imaginary part of the dielectric function due to direct inter-band transitions is given by the expression:

where Ω , ω , u, v and c are the unit-cell volume, photon frequencies, the vector defining the polarization of the incident electric field, valence and conduction bands, respectively. The real part of the dielectric function is obtained from ε_2 by a Kramers-Kronig transformation:

The refractive index $n(\omega)$ can be obtained based on ε_1 and ε_2 .

In calculation of the static $\chi^{(2)}$ coefficients, the so-called length-gauge formalism derived by Aversa and Sipe¹⁰ and modified by Rashkeev et al¹¹ is adopted, which has been proved to be successful in calculating the second order susceptibility for semiconductors and insulators.^{12–15} In the static case, the imaginary part of the static second-order optical susceptibility can be expressed as: χ^{abc} = $\frac{e^3}{h^2\Omega} \sum_{nml,k} \frac{r_{nm}^a (r_{ml}^b r_{ln}^c + r_{ml}^c r_{ln}^b)}{2\omega_{nm} \omega_{nl} \omega_{ln}} [\omega_n f_{ml} + \omega_m f_{ln} + \omega_l f_{nm}]$ + $\frac{ie^3}{4h^2\Omega} \sum_{nmk} \frac{f_{nm}}{\omega_{nm}^2} [r_{nm}^a (r_{mn;c}^b + r_{nm}^c) + r_{nm}^b (r_{mn;c}^a + r_{nm;a}^c) + r_{nm}^c (r_{mn;b}^a + r_{mn;a}^b)]$

where *r* is the position operator, $\hbar \omega_{nm} = \hbar \omega_n - \hbar \omega_m$ is the energy difference for the bands *m* and *n*, $f_{mn} = f_m - f_n$ is the difference of the Fermi distribution functions, subscripts *a*, *b*, and *c* are Cartesian indices, and $r^b_{mn;a}$ is the so-called generalized derivative of the coordinate operator in *k* space,

$$r_{nm;a}^{b} = \frac{r_{nm}^{a} \Delta_{mn}^{b} + r_{nm}^{b} \Delta_{mn}^{a}}{\omega_{nm}} + \frac{i}{\omega_{nm}} \times \sum_{l} (\omega_{lm} r_{nl}^{a} r_{lm}^{b} - \omega_{nl} r_{nl}^{b} r_{lm}^{a}) \qquad(4)$$

where $\Delta^{a}_{nm} = (p^{a}_{nn} - p^{a}_{mm}) / m$ is the difference between the electronic velocities at

the bands *n* and *m*.

As the nonlinear optical coefficients are sensitive to the momentum matrix, much finer k-point grid and large amount of empty bands are required to obtain a convergent $\chi^{(2)}$ coefficient. The $\chi^{(2)}$ coefficients here were calculated from PBE wavefunctions with a 7×3×1 k-point grid and about 300 empty bands. A scissor operator has been added to correct the conduction band energy (corrected to the experimental gap), which has been proved to be reliable in predicting the second order susceptibility for semiconductors and insulators.^{16–18}



Fig. S1 PXRD patterns of MOF-FJ1.



Fig. S2 View of π - π interactions within MOF-FJ1.





Fig. S4 TG curve of MOF-FJ1.



Fig. S5 UV-vis diffuse reflectance spectrum of MOF-FJ1.



Figure S6. Solid-state luminescence spectra of MOF-FJ1.

Electronic Supplementary Information (ESI)

MOFs ^a	2 nd ligand	Space Group	Dimension	Symmetry ^b	Ref.
$[Cd(bct)(H_2O)] \cdot H_2O$	No	$P\bar{1}$	2D	CS	10
[Zn(bct)(bip)]·2H ₂ O	bip	C2/c	3D	CS	19
[Mn ₃ (bct) ₃ (phen) ₂]·H ₂ O	phen	$P\bar{1}$	2D	CS	
$[Zn_4(bct)_2(\mu_2-O)_2(H_2O)_5] \cdot 2H_2O$	No	Сс	2D	NCS	20
$[Cd(bct)(H_2O)_2]$ ·3H ₂ O	No	P1	1D	CS	20
[Cu(bct)(phen)(H ₂ O)]·H ₂ O	phen	$P2_{1}/c$	1D	CS	
$[Ln_2(HCOO)_2(bct)_2] \cdot H_2O$	HCOO-	Pnma	3D	CS	21
$[Ln(bct)(OAc)(H_2O)]$ ·(H_2O)	CH ₃ COO ⁻	$P2_{1}/c$	3D	CS	22
$[Cd(bct)(bip)] \cdot 2(H_2O)$	bip	C2/c	3D	CS	23
$[Ni(bct)(bimb)_{3/2}(H_2O)_2] \cdot H_2O$	bimb	$P2_{1}/c$	2D	CS	24
$[M_5(\mu_2-H_2O)_2(\mu_3-OH)_2(bct)_4(H_2O)_8] \cdot 4H_2O$	No	$P2_{1}/n$	1D	CS	
$[Cd_2(bct)_2(bipy)] \cdot 5H_2O$	bipy	$P2_{1}/c$	2D	CS	25
[Cd(bct)(tib)]·H ₂ O·DMF	tib	P1	2D	CS	
$[Zn(bct)(H_2O)_2]$	No	$P2_{1}2_{1}2_{1}$	1D	NCS	This work

Table S1. Structure comparison in the reported MOFs with bct²⁻ ligand.

^abip = 1,4-bis(imidazol-1-ylmethyl)benzene

phen = 1,10-phenanthroline

bimb = 4,4'-bis(imidazol-1-ylmethyl) biphenyl

bipy = 4,4'-bipyridine

tib = 1,3,5-tris(1-imidazolyl)benzene

^bCS = centrosymmetric; NCS = non-centrosymmetric.

Identification code	MOF-FJ1		
Empirical formula	$C_{16}H_{13}N_{3}O_{6}Zn$		
Formula weight	408.66		
Crystal system	orthorhombic		
Space group	P2 ₁ 2 ₁ 2 ₁		
a/Å	4.9797(4)		
b/Å	11.2729(11)		
c/Å	27.335(3)		
$\alpha/^{\circ}$	90		
$eta/^{\circ}$	90		
γ/°	90		
Volume/Å ³	1534.5(3)		
Ζ	4		
$\rho_{\rm calc} {\rm g/cm}^3$	1.769		
μ/mm^{-1}	1.644		
<i>F</i> (000)	832		
Reflections collected	13295		
Unique reflections	3519		
Goodness-of-fit	0.88		
Final R_1^a indexes [I>=2 σ (I)]	0.0414		
Final $wR_{2^{b}}$ indexes [I>=2 σ (I)]	0.0667		
Flack parameter	0.057(13)		

Table S2. Crystal data and structure refinements for MOF-FJ1.

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, \ {}^{b}wR = (\Sigma (w(F_{o}{}^{2} - F_{c}{}^{2})^{2}) / \Sigma (w(F_{o}{}^{2})^{2}))^{1/2}$

MOF-FJ1			
Zn101	1.966(3)	C4–C5	1.386(6)
Zn1–O3 ¹	2.019(3)	C5–C6	1.403(6)
Zn1–O5W	1.989(3)	C5–C8	1.451(6)
Zn1–O6W	1.976(4)	C6–C7	1.380(6)
N1-C8	1.364(6)	C9–C10	1.453(6)
N1-C9	1.332(6)	C10-C11	1.385(6)
N2-N3	1.354(5)	C10–C15	1.389(7)
N2C9	1.342(5)	C11–C12	1.385(6)
N3–C8	1.342(6)	C12–C13	1.381(6)
C1–C2	1.503(7)	C13–C14	1.379(6)
C1–O2	1.237(6)	C13–C16	1.489(7)
C101	1.294(5)	C14–C15	1.377(7)
C2–C3	1.380(6)	C16-O3	1.287(6)
С2-С7	1.390(6)	C16-O4	1.239(6)
C3–C4	1.386(6)	O1–Zn1–O3 ¹	99.84(14)
O1–Zn1–O5W	99.90(14)	C6C7C2	120.1(5)
O1–Zn1–O6W	133.05(17)	N1-C8-C5	125.2(5)
O5W–Zn1–O31	138.72(16)	N3-C8-N1	113.4(4)
O6W–Zn1–O31	99.15(16)	N3-C8-C5	121.5(5)
O6W-Zn1-O5W	93.19(15)	N1-C9-N2	109.5(4)
C9-N1-C8	103.8(4)	N1-C9-C10	128.2(4)
C9-N2-N3	110.5(4)	N2-C9-C10	122.3(4)
C8-N3-N2	102.8(4)	C11-C10-C9	120.5(5)
O2–C1–C2	123.0(5)	C11-C10-C15	118.7(5)
O2C1O1	121.5(5)	C15-C10-C9	120.8(5)
O1–C1–C2	115.4(4)	C10-C11-C12	120.3(5)
C3-C2-C1	121.3(4)	C13-C12-C11	120.8(5)
С3-С2-С7	118.9(5)	C12-C13-C16	120.4(5)
C7–C2–C1	119.8(5)	C14-C13-C12	118.8(5)
C2–C3–C4	121.1(5)	C14-C13-C16	120.8(5)
C3-C4-C5	120.8(5)	C15-C14-C13	120.8(5)
C4-C5-C6	117.7(5)	O3-C16-C13	117.4(5)
C4–C5–C8	121.6(4)	O4-C16-C13	122.0(5)
C6–C5–C8	120.6(4)	O4C16O3	120.6(5)
С7–С6–С5	121.4(4)	C14–C15–C10	120.6(5)

 Table S3. Selected bond lengths (Å) and angles (°).

¹1/2–X, 2–Y, –1/2+Z

D—H…A	d(D—H)	$d(H \cdots A)$	$d(D \cdots A)$	D—H…A	
N2–H2…O4 ¹	0.86	2.1	2.798(6)	137.9	
O5W−H5WA…O4 ²	0.86	2.01	2.694(5)	135.6	
O5W−H5WB…O4 ³	0.86	1.96	2.738(5)	150.7	
O6W−H6WA…O4 ⁴	0.85	1.98	2.803(5)	161.1	
O6W−H6WB…O4 ⁵	0.75(5)	1.89(5)	2.639(5)	173(7)	
¹ 2-X, -1/2+Y, 1/2-Z; ² -3/2+X, 3/2-Y, -Z; ³ -1+X, +Y, +Z; ⁴ -1/2-X, 2-Y, -1/2+Z;					

Electronic Supplementary Information (ESI)

Table S4. Geometrical parameters (Å, °) of selected hydrogen bonds for MOF-FJ1.

⁵–1/2+X, 5/2–Y, –Z

Table S5. Calculated \sum values of several 1D NLO MOFs.

MOFs ^a	space group	calculated	SHG	ref
		Σ	$(I^{2\omega})$	
$[Zn(bpp)(C_6H_5COO)_2] \cdot 2H_2O$	Aba2	36.47°	< KDP	26
$[Zn(L)_2(H_2O)]_2 \cdot CH_3CN \cdot 3H_2O$	Fdd2	47.9°	$75 \times \alpha$ -quartz	27
$[Zn(peba)_2]$	$P2_{1}2_{1}2_{1}$	56.67°	$2 \times KDP$	28
$[Zn_2(bpp)(pht)_2]$	Cc	60.08°	$2 \times KDP$	29
[Zn(bct)(H ₂ O) ₂] (MOF-FJ1)	$P2_{1}2_{1}2_{1}$	98.47°	$3.5 \times \text{KDP}$	This work

 $^{a}bpp = 1,3-bis(4'-pyridyl)propane;$ L = 4-[2-(4'-pyridyl)ethenyl]cinnamate; Hpeba

= 3-(2-(2'-pyridyl)) ethenyl) benzoic acid; $H_2pht = 1,2$ -benzenedicarboxylate acid.

REFERENCES

- [1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341.
- [2] G. M. Sheldrick, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 2015, 71, 3-8.
- [3] A. L. Spek, Acta Crystallogr., Sect D: Biol. Crystallogr. 2009, 65, 148–155.
- [4] G. Kresse, VASP, 5.3.5; http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html, 2014.
- [5] G. Kresse, J. Furthmuller, Phys. Rev. B: Condens. Matter 1996, 54, 11169–11186.
- [6] G. Kresse, D. Joubert, Phys. Rev. B: Condens. Matter 1999, 59, 1758–1775.
- [7] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865–3868.
- [8] P. E. Blochl, Phys. Rev. B: Condens. Matter 1994, 50, 17953–17979.
- [9] H. J. Monkhorst, J. D. Pack, Phys. Rev. B: Condens. Matter 1976, 13, 5188.
- [10]C. Aversa, J. E. Sipe, *Phys. Rev. B* 1995, 52, 14636–14645.
- [11]S. N. Rashkeev, W. R. L. Lambrecht, B. Segall, Phys. Rev. B 1998, 57, 3905.
- [12] J. Hu, Z. Ma, J. Li, C. He, Q. Li, K. Wu, J. Phys. Appl. Phys. 2016, 49, 85103– 85103.
- [13] J. Li, Z. Ma, C. He, Q. Li, K. Wu, J. Mater. Chem. C 2016, 4, 1926–1934.
- [14] Z. Ma, K. Wu, R. Sa, K. Ding, Q. Li, Aip Advances 2012, 2, 032170.
- [15] Z. Ma, K. Wu, R. Sa, Q. Li, Y. Zhang, J. Alloy. Compd. 2013, 568, 16-20.
- [16]B. Champagne, D. M. Bishop, Adv. Chem. Phys. 2003, 126, 41-92.
- [17] A. H. Reshak, S. Auluck, I. V. Kityk, Phys. Rev. B 2007, 75, 245120.
- [18]Y.-Z. Huang, L.-M. Wu, X.-T. Wu, L.-H. Li, L. Chen, Y.-F. Zhang, J. Am. Chem.
- Soc. 2010, 132, 12788–12789.

- [19] X.-Y. Hou, X. Wang, F. Fu, J.-J. Wang, L. Tang, J. Coord. Chem., 2013, 66, 3126–3136
- [20] M. Yu, M. Hu, Z. Wu, RSC Adv., 2013, 3, 25175-25183
- [21] S. Wang, J. Xu, Y. Fan, J. Jia, L. Gao, J. Sun, L. Shan, X. Chen, L. Wang, H. J.
 Seo, *RSC Adv.*, **2015**, *5*, 106107–106112
- [22] X. Hou, X. Wang, H. Wang, L. Gao, F. Fu, J. Wang, L. Tang, J. Cao, J. Coord. Chem., 2015, 68, 1814–1828
- [23] H. Xiang-Yang, W. Xiao, R. Yi-Xia, W. Ji-Jiang, J. Wei, K. Wei-Wei, M. Xin, H. Xing-Xing, *Chinese J. Struct. Chem.*, 2017, 36, 2067–2072
- [24] Q. Hu, L. Qin, J. Lei, X.-X. Tan, G. Ni, Y.-Q. Wang, J. Li, F.-H. Cao, *Polyhedron*, **2018**, *151*, 33–36
- [25] Y.-X. Zhang, H. Lin, Y. Wen, Q.-L. Zhu, Cryst. Growth Des., 2019, 19, 1057– 1063.
- [26] Y.-Q. Zheng, J. Zhang, J.-Y. Liu, CrystEngComm. 2010, 12, 2740-2748.
- [27]P. Ayyappan, G. Sirokman, O. R. Evans, T. H. Warren, W. Lin, *Inorg. Chim.* Acta 2004, 357, 3999–4004.
- [28] T. Hang, D.-W. Fu, Q. Ye, R.-G. Xiong, Cryst. Growth Des. 2009, 9, 2026–2029.
- [29]Y.-B. Chen, J. Zhang, J.-K. Cheng, Y. Kang, Z.-J. Li, Y.-G. Yao, *Inorg. Chem. Commun.* 2004, 7, 1139–1141.