Inorganic Chemistry

Cite This: Inorg. Chem. XXXX, XXX, XXX−XXX

Communication

pubs.acs.org/IC

Nonlinear-Optical Behaviors of a Chiral Metal−Organic Framework Comprised of an Unusual Multioriented Double-Helix Structure

Xiaoli Huang,[†,‡] Qiyang Li,[†,‡] Xue Xiao,[†] Shuping Jia,[†] Yue Li,[†] Zhigang Duan,[†] Lei Bai,[†] Ze Yuan,[†] Lin Li,[†] Zhihua Lin,[*,§] and Yonggang Zhao[*,†]

[†]Key Laboratory of Flexible Electronics (KLOFE), Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), and [§]College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, P. R. China

Supporting Information

ABSTRACT: We present here the synthesis of one enantiomeric pair of metal−organic framework materials comprised of a unique multioriented double-helix structure from an achiral spirocenter ligand. Our study clearly shows that the chiral MOF material encompasses concurrently multiple nonlinear-optical functions in the solid state: the noncentrosymmetric structural feature brings the chiral MOF high second-harmonic-generation efficiency; the incorporation of the spirocenter ligand can efficiently produce two-photon-excited photoluminescence with a larger-action cross-sectional value.

The development of materials with nonlinear-optical (NLO) functions continues to receive researchers' attention because of the key role of NLO materials in laser and biomedical imaging technologies.[1−3] Although there has been tremendous interest in the construction of NLO materials, such as organic chromophores, polymers, semiconducting materials, and quantum dots, the goal of manipulating the NLO properties of the materials is still of great challenge. In the last 2 decades, extensive research on metal−organic frameworks (MOFs) have shown that they possess numerous advantages over conventional materials, including, but not limited to, structural tunability, stability, cost-efficient fabrication, and ease of synthesis on a large bulk scale.[4−7] In particular, their optical properties can be systematically tailored by suitable choices of the metal and ligand constituents, from which the performance of the MOFs can be significantly improved to enable viable NLO applications.[8−11]

To date, intensive studies have been performed on MOF-based NLO materials, particularly in the second harmonic generation (SHG).[12−14] In principle, noncentrosymmetric organization is a prerequisite for SHG processes in a bulk material. To produce noncentrosymmetric MOFs with high SHG, several strategies have been successfully used, including the use of chiral ligands,[15,16] construction of diamondoid[17,18] or octupolar structures,[19,20] utilizing the structural defects,[21,22] control of the degree of interpenetration,[23] etc. Compared with the well-documented SHG-active frameworks, MOFs with simultaneous two-photon or multiphoton absorption by the incorporation of NLO-active organic linkers[24−27] or the encapsulation of suitable dyes in the voids of the MOFs[28,29] have only recently been reported and have shown potential applications in lasing,[30] three-dimensional (3D) patterning, and data storage.[31] Recent success in MOF-based NLO materials has encouraged us to explore the noncentrosymmetric structures with respect to their multiple optical nonlinearities.

In the design of NLO materials, π-conjugated organic molecules with low dielectric constants, variable spectral characteristics, and fast NLO response occupy a prominent position, among which molecules containing spirobifluorene units are a promising class of conjugated systems. The rigidity of the spirobifluorene units can increase the effective π-electron conjugation and suppress nonradiative deactivation pathways, leading to high photoluminescence (PL) quantum yields. Moreover, the chemical versatility of (spiro)molecules allows modulation of the π-conjugation length within a multipolar structure for enhanced polarization of charge delocalization, which is beneficial for the NLO performance.

By employing an achiral spirocenter ligand,[32−34] 4,4′,4′′,4‴-(9,9′-spirobifluorene-2,2′,7,7′-tetrayl)tetrabenzoic acid (H_4L),[35,36] we report one enantiomeric pair of 3D MOFs (**IAM-1M**/**1P**; IAM = Institute of Advanced Materials) comprised of unusual double-helix structure in this study. Associated with the noncentrosymmetric feature of the structure, chiroptical properties such as circular dichroism (CD), together with the high SHG activity, are described. Moreover, enhanced two-photon-excited fluorescence (2PEF) is also observed for the MOF material compared with its spirobifluorene-based ligand.

Structural analysis revealed that the single crystals in one batch of **IAM-1** contain **1M** and its enantiomorph **1P**, with chiral space groups of $P3_121$ and $P3_221$, respectively. **IAM-1** is constructed from dinuclear zinc(II) building units with four bridging ligands (Figure 1). A remarkable feature of **IAM-1** is their double-helix arrangements. The spirocenter lignads are interconnected through the dizinc(II) units to generate the left-handed double-helical chain in **1M** and the right-handed helix in **1P**, with pitches of 16.992(3) Å for **1M** and 17.048(7) Å for **1P** (Figure 2). The most striking feature of the structure is that **IAM-1** is comprised of three structurally identical double-helical chains with the same handedness but different orientations along the (1, 0, 0), (0, 1, 0) and (1, 1, 0) axes, respectively (Figure 1b). All three helical chains are parallel to the *ab* plane and propagate along different directions orthogonal to a 3_1 screw axis. The double-helical chains with the same orientation are parallel to each other in the *ab* plane, while the neighboring double-helical

Received: March 16, 2018

DOI: 10.1021/acs.inorgchem.8b00671
Inorg. Chem. XXXX, XXX, XXX−XXX

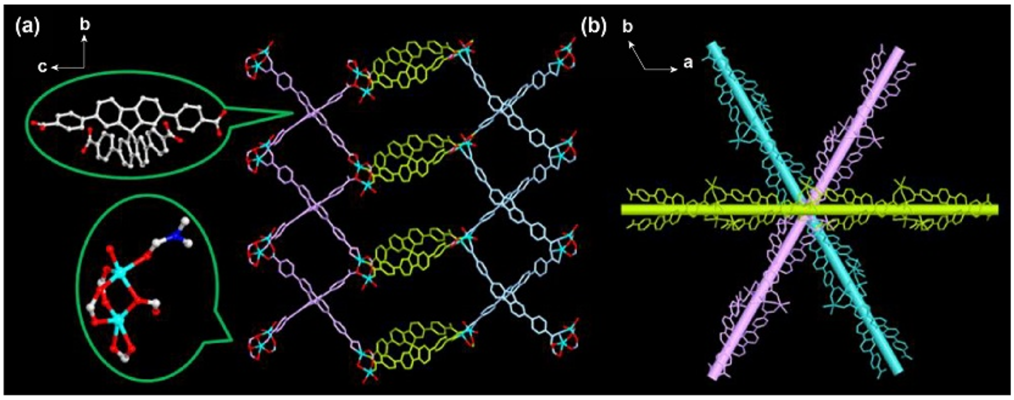

Figure 1. View of the spirobifluorene-based ligand and dizinc(II) building unit in **IAM-1M** (color code: Zn, turquoise; O, red; C, pale gray; N, blue) and the multioriented double-helical chains along the *a* axis (a) and *c* axis (b), in which lime, pale-blue, and lavender represent three helical chains along the (1, 0, 0), (0, 1, 0), and (1, 1, 0) axes, respectively. H atoms were omitted for clarity.

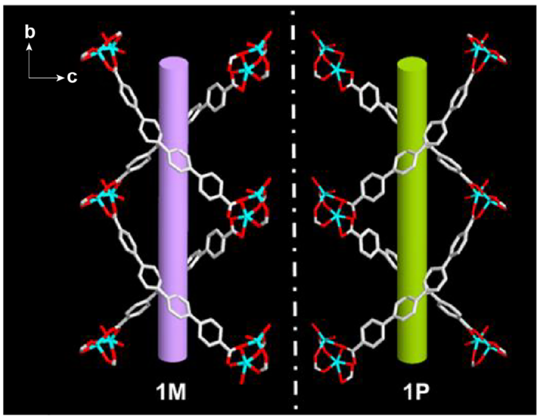

Figure 2. Left-handed (M) and right-handed (P) double-helical motifs composed of achiral ligands in the enantiomorphs **IAM-1M** and **IAM-1P**, respectively. H atoms were omitted for clarity.

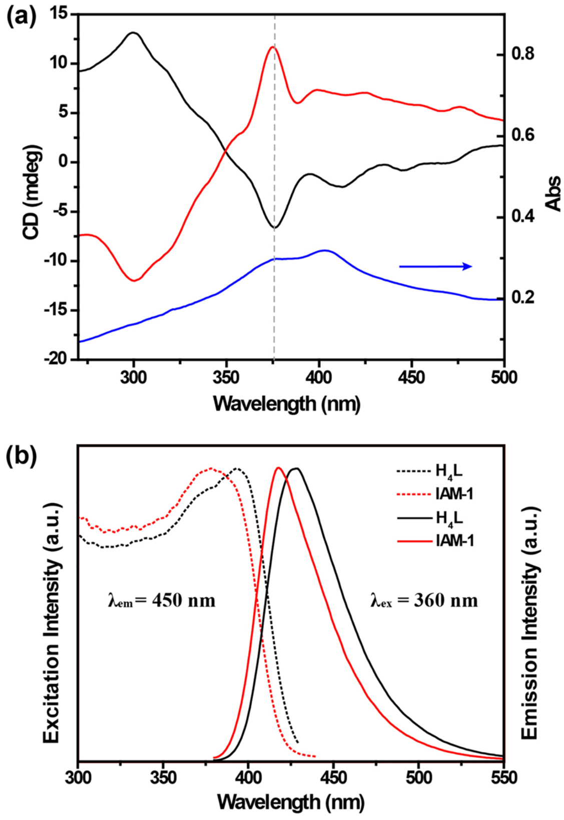

Figure 3. (a) CD spectra of **IAM-1M** and **IAM-1P** and UV−vis absorption of a bulk sample of **IAM-1** (blue) in *N*,*N*-dimethylformamide. (b) Solid-state excitation and fluorescence spectra of H_4L and **IAM-1**.

chains with different orientations are alternately arranged and coupled to each other by sharing the dizinc(II) units, giving rise to a 3D framework of **IAM-1**. Notably, because of the same handedness of the three helical chains, the whole structure is homochiral. To the best of our knowledge, the previously reported single- or double-helical MOF structures are all comprised of helixes in a parallel fashion, whereas the structure of **IAM-1** encompassing concurrently multioriented but structurally identical double-helical chains has not been reported before. Moreover, additional independent equivalent frameworks are present in **IAM-1** in order to stabilize the whole structure, affording a 2-fold interpenetrating framework. It is worth noting that, because of the interpenetration, a comparably dense packing of the organic linker in **IAM-1** was achieved, with a chromophore linker concentration of 0.86 mol dm^{-3}. From a topological point of view, both the dizinc(II) unit and the ligand can be reduced to the 4-connected node to give a 4,4-connected network with qzd topology and the point symbol of $\{4^2\ 8^4\}$.

To verify the occurrence of spontaneous resolution during the crystal growth, CD spectra were performed. A total of 20 randomly picked individual crystals from one batch were tested. As anticipated, CD spectra showed the opposite Cotton effect (positive or negative) varying from crystal to crystal, indicating that either **1M** or **1P** formed under spontaneous resolution (Figure 3a). The CD spectral data reveal that **IAM-1** crystallizes as a racemic mixture of enantiomerically pure crystals of one enantiomeric form (**M**) and its opposite form (**P**) in a ratio of nearly 50:50.

As is well-known, spirobifluorene derivatives are a class of efficient blue-light-emitting materials. The one-photon-excited fluorescence spectra show strong blue emissions for the ligand H_4L around 428 nm and **IAM-1** around 418 nm in the solid state (Figure 3b), with the absolute quantum yields ($\Phi_{a,f}$) of 33.62% and 46.67%, respectively, suggesting excellent PL characteristics for both.

In view of the noncentrosymmetric structural feature of **IAM-1**, its NLO behavior was studied with the use a confocal laser scanning microscope equipped with a Ti:sapphire laser (1064 nm output). The SHG efficiency of **IAM-1** was measured using the Kurtz−Perry method at room temperature.[37] Using a 1064 nm laser source through the treated microcrystalline sample (particle sizes of 75−150 μm), it was found that **IAM-1** displays a strong SHG efficiency (Figure 4), which is about 0.56 times that of $LiNdO_3$ in the same particle size, that is, an efficiency of 21 times that of KDP and 336 times that of α-quartz. To accurately investigate the effective SHG of **IAM-1**, measurements as a function of the particle size were performed. As shown in Figure 4, the SHG efficiency of **IAM-1** keeps increasing as the particle size increases, indicating that the material is phase-matchable (PM).[11] By using the well-known PM material $LiNbO_3$ as the reference, the effective SHG (d_{eff}) of **IAM-1** was determined to be 1.64 pm V^{-1}, that is, an efficiency of 0.37 times that of $LiNbO_3$, which is concordant with the comparison made on the SHG intensity.

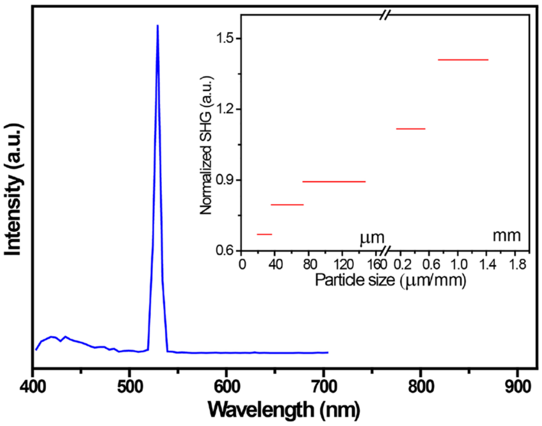

Figure 4. SHG spectra of **IAM-1**. Inset: Particle size versus SHG intensity for **IAM-1** showing the PM curve.

A confocal laser scanning microscope was subsequently used to study the 2PEF of **IAM-1** and its ligand at room temperature. Figure 5 clearly demonstrates bright upconverted PL when **IAM-1** was scanned and irradiated by a tunable femtosecond laser ranging from 690 to 770 nm, which corresponds to the 2PEF spectra. PL reached a maximum efficiency when excited at 720 nm, which is roughly located at half of the linear absorption peak energy. To quantify the 2PEF of the investigated samples, the two-photon-action cross section ($\eta\sigma_2$) was determined using perylene as a standard sample at the same laser wavelength and power. As shown in Figure S15, the $\eta\sigma_2$ value for **IAM-1** was found to be in the range of 2.13−6.78 GM with a maximum at 720 nm, which is comparable with the values reported for NLO MOF materials[24] and about 2 times larger than that of the ligand. This difference between IAM-1 and its ligand can mainly be attributed to their different fluorescence efficiency in the solid state, together with the high packing density of the NLO chromophore linker in the framework.[26] Furthermore, the third-order two-photon upconversion was confirmed by the slope of PL plotted as a function of the excitation intensity on the log-to-log scale, which was found to be ≈2.

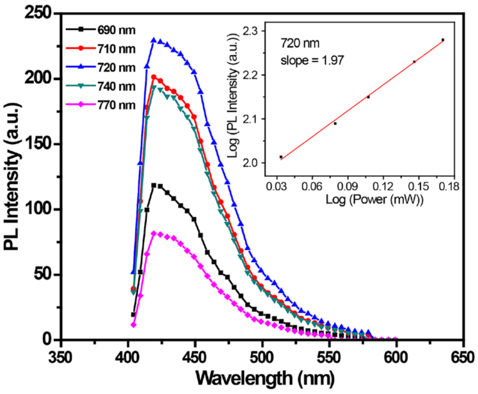

Figure 5. Two-photon-excited emission spectra of **IAM-1** depending on different excitation wavelengths. The inset shows the two-photon-excited PL intensity dependence on the laser intensity at 720 nm.

In conclusion, using an achiral spirocenter ligand, we reported a chiral 3D MOF material, **IAM-1**, comprised of an extraordinary multioriented double-helix structure in this work. The enantiomeric pairs (**1M** and **1P**) assembled by spontaneous resolution have been successfully separated. This study shows the successful integration of multiple NLO behaviors within one chiral MOF structure: the noncentrosymmetric feature of the structure brings the chiral MOF high SHG efficiency; the incorporation of the spirocenter ligand into the framework can efficiently produce two-photon-excited PL with a larger-action cross-sectional value compared with the organic linker.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b00671.

> Synthetic routes to the ligand, powder X-ray diffraction, thermogravimetric analysis, structure analysis, CD, PL, SHG, and 2PEF spectra and analysis, and crystal data (PDF)

Accession Codes

CCDC 1817958−1817959 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: linzh@njtech.edu.cn (Z.L.).
*E-mail: iamygzhao@njtech.edu.cn (Y.Z.).

ORCID

Yonggang Zhao: 0000-0002-0357-382X

Author Contributions

‡These authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Grants 21471079 and 21501092) and the Natural Science Foundation of Jiangsu Province for Youth (Grant BK20140928).

■ REFERENCES

(1) *Nonlinear Optical Effects and Materials*; Günter, P. , Ed.; Springer: Heidelberg, 2000.

(2) Boyd, R. W. *Nonlinear Optical*, 3rd ed.; Academic Press, 2008.
(3) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley Classics Library, 2003.
(4) Li, B.; Wen, H. M.; Cui, Y.; Zhou, W.; Qian, G.; Chen, B. Emerging Multifunctional Metal-Organic Framework Materials. *Adv. Mater.* **2016**, *28*, 8819−8860.
(5) Furukawa, H. C.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The Chemistry and Applications of Metal-Organic Frameworks. *Science* **2013**, *341*, 1230444.
(6) Zhou, H.-C.; Kitagawa, S. Metal−Organic Frameworks (MOFs). *Chem. Soc. Rev.* **2014**, *43*, 5415−5418.
(7) Cui, Y.; Li, B.; He, H.; Zhou, W.; Chen, B.; Qian, G. Metal-Organic Frameworks as Platforms for Functional Materials. *Acc. Chem. Res.* **2016**, *49*, 483−93.
(8) Wang, C.; Liu, D.; Lin, W. Metal−Organic Frameworks as A Tunable Platform for Designing Functional Molecular Materials. *J. Am. Chem. Soc.* **2013**, *135*, 13222−13234.
(9) Medishetty, R.; Zareba, J. K.; Mayer, D.; Samoc, M.; Fischer, R. A. Nonlinear Optical Properties, Upconversion and Lasing in Metal-Organic Frameworks. *Chem. Soc. Rev.* **2017**, *46*, 4976−5004.
(10) Mingabudinova, L. R.; Vinogradov, V. V.; Milichko, V. A.; Hey-Hawkins, E.; Vinogradov, A. V. Metal-Organic Frameworks as Competitive Materials for Non-Linear Optics. *Chem. Soc. Rev.* **2016**, *45*, 5408−5431.
(11) Ok, K. M.; Chi, E. O.; Halasyamani, P. S. Bulk Characterization Methods for Non-centrosymmetric Materials: Second-Harmonic Generation, Piezoelectricity, Pyroelectricity, and Ferroelectricity. *Chem. Soc. Rev.* **2006**, *35*, 710−717.
(12) Evans, O. R.; Lin, W. Crystal Engineering of NLO Materials Based on Metal−Organic Coordination Networks. *Acc. Chem. Res.* **2002**, *35*, 511−522.
(13) Wang, C.; Zhang, T.; Lin, W. Rational Synthesis of Non-centrosymmetric Metal-Organic Frameworks for Second-Order Non-linear Optics. *Chem. Rev.* **2012**, *112*, 1084−1104.
(14) Yu, J.; Cui, Y.; Wu, C.; Yang, Y.; Wang, Z.; O'Keeffe, M.; Chen, B.; Qian, G. Second-Order Nonlinear Optical Activity Induced by Ordered Dipolar Chromophores Confined in the Pores of an Anionic Metal-Organic Framework. *Angew. Chem., Int. Ed.* **2012**, *51*, 10542−10545.
(15) Anthony, S. P.; Radhakrishnan, T. P. Helical and Network Coordination Polymers Based on a Novel C2-symmetric Ligand: SHG Enhancement through Specific Metal Coordination. *Chem. Commun.* **2004**, *9*, 1058−1059.
(16) Huang, Q.; Yu, J.; Gao, J.; Rao, X.; Yang, X.; Cui, Y.; Wu, C.; Zhang, Z.; Xiang, S.; Chen, B.; Qian, G. Two Chiral Nonlinear Optical Coordination Networks Based on Interwoven Two-Dimensional Square Grids of Double Helices. *Cryst. Growth Des.* **2010**, *10*, 5291−5296.
(17) Evans, O. R.; Xiong, R.-G.; Wang, Z.; Wong, G. K.; Lin, W. Crystal Engineering of Acentric Diamondoid Metal−Organic Coordination Networks. *Angew. Chem., Int. Ed.* **1999**, *38*, 536−538.
(18) Lin, J.-D.; Long, X.-F.; Lin, P.; Du, S.-W. A Series of Cation-Templated, Polycarboxylate-Based Cd(II) or Cd(II)/Li(I) Frameworks with Second-Order Nonlinear Optical and Ferroelectric Properties. *Cryst. Growth Des.* **2010**, *10*, 146−157.
(19) Lin, W.; Wang, Z.; Ma, L. A Novel Octupolar Metal-Organic NLO Material Based on a Chiral 2D Coordination Network. *J. Am. Chem. Soc.* **1999**, *121*, 11249−11250.
(20) Liu, Y.; Li, G.; Li, X.; Cui, Y. Cation-Dependent Nonlinear Optical Behavior in an Octupolar 3D Anionic Metal−Organic Open Framework. *Angew. Chem.* **2007**, *119*, 6417−6420.
(21) Van Cleuvenbergen, S.; Stassen, I.; Gobechiya, E.; Zhang, Y.; Markey, K.; De Vos, D. E.; Kirschhock, C.; Champagne, B.; Verbiest, T.; van der Veen, M. A. ZIF-8 as Nonlinear Optical Material: Influence of Structure and Synthesis. *Chem. Mater.* **2016**, *28*, 3203−3209.
(22) Liu, M.; Quah, H. S.; Wen, S.; Wang, J.; Kumar, P. S.; Eda, G.; Vittal, J. J.; Ji, W. Nonlinear Optical Properties of a One-dimensional Coordination Polymer. *J. Mater. Chem. C* **2017**, *5*, 2936−2941.
(23) Evans, O. R.; Lin, W. Crystal Engineering of Nonlinear Optical Materials Based on Interpenetrated Diamondoid Coordination Networks. *Chem. Mater.* **2001**, *13*, 2705−2712.
(24) Quah, H. S.; Chen, W.; Schreyer, M. K.; Yang, H.; Wong, M. W.; Ji, W.; Vittal, J. J. Multiphoton Harvesting Metal-Organic Frameworks. *Nat. Commun.* **2015**, *6*, 7954.
(25) Medishetty, R.; Nalla, V.; Nemec, L.; Henke, S.; Mayer, D.; Sun, H.; Reuter, K.; Fischer, R. A. A New Class of Lasing Materials: Intrinsic Stimulated Emission from Nonlinear Optically Active Metal-Organic Frameworks. *Adv. Mater.* **2017**, *29*, 1605637−1605637.
(26) Medishetty, R.; Nemec, L.; Nalla, V.; Henke, S.; Samoc, M.; Reuter, K.; Fischer, R. A. Multi-Photon Absorption in Metal−Organic Frameworks. *Angew. Chem., Int. Ed.* **2017**, *56*, 14743−14748.
(27) Liu, M.; Quah, H. S.; Wen, S.; Yu, Z.; Vittal, J. J.; Ji, W. Efficient Third Harmonic Generation in a Metal−Organic Framework. *Chem. Mater.* **2016**, *28*, 3385−3390.
(28) He, H.; Ma, E.; Cui, Y.; Yu, J.; Yang, Y.; Song, T.; Wu, C. D.; Chen, X.; Chen, B.; Qian, G. Polarized Three-Photon-Pumped Laser in a Single MOF Microcrystal. *Nat. Commun.* **2016**, *7*, 11087.
(29) Yu, J.; Cui, Y.; Xu, H.; Yang, Y.; Wang, Z.; Chen, B.; Qian, G. Confinement of Pyridinium Hemicyanine Dye within an Anionic Metal-Organic Framework for Two-Photon-Pumped Lasing. *Nat. Commun.* **2013**, *4*, 2719.
(30) He, H.; Ma, E.; Yu, J.; Cui, Y.; Lin, Y.; Yang, Y.; Chen, X.; Chen, B.; Qian, G. Periodically Aligned Dye Molecules Integrated in a Single MOF Microcrystal Exhibit Single-Mode Linearly Polarized Lasing. *Adv. Opt. Mater.* **2017**, *5*, 1601040.
(31) Yu, J.; Cui, Y.; Wu, C. D.; Yang, Y.; Chen, B.; Qian, G. Two-Photon Responsive Metal-Organic Framework. *J. Am. Chem. Soc.* **2015**, *137*, 4026−4029.
(32) Gao, E.-Q.; Yue, Y.-F.; Bai, S.-Q.; He, Z.; Yan, C.-H. From Achiral Ligands to Chiral Coordination Polymers: Spontaneous Resolution, Weak Ferromagnetism, and Topological Ferrimagnetism. *J. Am. Chem. Soc.* **2004**, *126*, 1419−1429.
(33) Bisht, K. K.; Suresh, E. Spontaneous Resolution to Absolute Chiral Induction: Pseudo-Kagomé Type Homochiral Zn(II)/Co(II) Coordination Polymers with Achiral Precursors. *J. Am. Chem. Soc.* **2013**, *135*, 15690−15693.
(34) Chen, N.; Li, M.-X.; Yang, P.; He, X.; Shao, M.; Zhu, S.-R. Chiral Coordination Polymers with SHG-Active and Luminescence: An Unusual Homochiral 3D MOF Constructed from Achiral Components. *Cryst. Growth Des.* **2013**, *13*, 2650−2660.
(35) Moreau, F.; Audebrand, N.; Poriel, C.; Moizan-Baslé, V.; Ouvry, J. A 9,9′-Spirobifluorene Based Metal-Organic Framework: Synthesis, Structure Analysis and Gas Sorption Properties. *J. Mater. Chem.* **2011**, *21*, 18715−18722.
(36) Park, H. J.; Jang, J. K.; Kim, S. Y.; Ha, J. W.; Moon, D.; Kang, I. N.; Bae, Y. S.; Kim, S.; Hwang, D. H. Synthesis of a Zr-Based Metal-Organic Framework with Spirobifluorenetetrabenzoic Acid for the Effective Removal of Nerve Agent Simulants. *Inorg. Chem.* **2017**, *56*, 12098−12101.
(37) Kurtz, S. K.; Perry, T. T. A Powder Technique for the Evaluation of Nonlinear Optical Materials. *J. Appl. Phys.* **1968**, *39*, 3798−3813.