

A Journal of the Gesellschaft Deutscher Chemiker A DOCH International Edition Market Chemiker CDCh Chemiker Ch

Accepted Article

- Title: A 3D Anionic Metal Covalent Organic Framework with soc Topology Built from Octahedral Ti(IV) Complex for Photocatalytic Reactions
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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.202102665

Link to VoR: https://doi.org/10.1002/anie.202102665

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A 3D Anionic Metal Covalent Organic Framework with soc Topology Built from Octahedral Ti(IV) Complex for Photocatalytic Reactions

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Abstract: The construction of three-dimensional (3D) covalent organic frameworks (COFs) remains challenging due to the limited types of organic building blocks. With octahedral Ti(IV) complex as the building unit, this study reports on the first 3D anionic titanium-based COF (Ti-COF-1) with an edge-transitive (6, 4)-connected **soc** topology. Ti-COF-1 exhibits high crystallinity, superior stability, and large specific surface area (1000.4 m² g⁻¹). Moreover, Ti-COF-1 has a broad absorption band in the UV spectrum with an optical energy gap of 1.86 eV, and exhibits high photocatalytic activity toward Meerwein addition reactions. This research demonstrates an attractive strategy for the design of 3D functional COFs.

Covalent organic frameworks (COFs), a new class of crystalline porous materials with highly ordered framework structures, have attracted widespread attention for use in adsorption, separation, catalysis, and optoelectronics.^[1-3] Most of the reported COFs possess two-dimensional (2D) structures with interlayer noncovalent interactions to form one-dimensional pore channels.^[4] By contrast, three-dimensional (3D) COFs usually have interconnected porosity that ensures high accessible surface area and abundant active sites.^[5] However, the limited types of building blocks (mainly tetrahedral organic building units) restrict the development of 3D COFs. On the other hand, the introduction of metal ions into porous COFs to form metal covalent organic frameworks (MCOFs) may give clues for the construction of 3D COFs, as the metal coordination has a good spatial orientation.^[6] Recently, Yaghi group synthesized 3D MCOFs (COF-505 and COF-500) via the use of tetrahedral metal complex as 4-connected building unit.^[7] However, the development of new topologies for 3D COFs using metal complexes beyond tetrahedral configurations remains a substantial challenge.

This study develops a new strategy to construct 3D MCOFs with a new topology via the use of novel metal-complex building blocks. Metal-organic cages (MOCs) formed by metal ions and bridging chelate ligands usually have highly symmetric cage structures,^[8] making them good building blocks for MCOFs. As shown in Scheme. 1, cubic MOCs can be assembled from 3-connected C_3 -symmetric octahedral metal complexes and 4-connected planar units.^[9] If the vertices of cubic MOCs are decorated with linking groups, these MOCs can connect with each other to form 3D MCOFs. Based on this "MOC-to-MCOF" strategy, the as-synthesized 3D MCOFs can inherit the following advantages of MOCs, metal organic frameworks (MOFs) and

COFs: (1) high crystallinity: linked by coordinate bonds, the metal coordination centers may improve the crystallization of MCOFs; (2) high porosity: MCOFs not only inherit voids from MOCs but also have newly formed interconnected channels, which can enrich the porosity of COFs; (3) superior stability: by combining dynamic covalent bonds and coordinate bonds, MCOFs will be more stable; (4) tunable functionality: MCOFs will show promising applications in different areas, especially for catalysis, due to their abundant metal centers.



Scheme 1. The schematic illustration of the "MOC-to-MCOF" strategy for the construction of a 3D COF with **soc** topology.

To prove the "MOC-to-MCOF" strategy, a new C_3 -symmetric octahedral Ti(IV) complex Na₂Ti(2,3-DHTA)₃ (2,3-DHTA= 2,3-dihydroxyterephthalaldehyde) was designed as a 6-connected building unit, and an anionic 3D titanium-based COF (**Ti-COF-1**) with **soc** topology was then successfully constructed for the first time. In recent years, metal-catechol anionic MOCs have been widely used for catalysis.^[10] **Ti-COF-1** presents high charge

mobility, and is studied as promising catalyst for Meerwein addition reactions.

Na₂Ti(2,3-DHTA)₃ was synthesized by titanium oxide acetylacetonate and 2,3-DHTA in acetonitrile solution (Figure 1a; see SI). The precipitation of dark red crystals was achieved via the slow diffusion of isopropyl ether. X-ray single-crystal structure determination revealed that Ti(IV) center coordinated with six oxygen atoms from the three 2,3-DHTA ligands, forming an octahedral TiO₆ coordination geometry, with an average Ti-O bond length of 1.966 Å (Figure 1b and Table S4).^[11] The six aldehyde groups of Na₂Ti(2,3-DHTA)₃ were found to be oriented in six different directions with C_3 symmetry, suggesting that Ti(2,3-DHTA)₃²⁻ could be used as an octahedral building unit to construct 3D MCOFs.

Ti-COF-1 was synthesized via an imine condensation reaction between Na₂Ti(2,3-DHTA)₃ and 4, 4', 4", 4"'-(pyrene-1, 3, 6, 8-tetrayl)tetraaniline (PyTTA) with 6 M acetic acid as a catalyst in a mixture of o-dichlorobenzene, mesitylene and acetonitrile at 120 °C for 7 d (Figure 1c; see SI). The FT-IR spectrum of Ti-COF-1 (Figure 2a) revealed significantly weakened signals from C=O vibration (1660 cm⁻¹) and the appearance of a C=N bond (1610 cm⁻¹). The solid-state ¹³C cross-polarization magic-angle-spinning (CP/MAS) NMR spectrum of Ti-COF-1 was then collected. A resonance signal at 158 ppm from the carbon in the C=N group was observed (Figure 2b). The ultraviolet/visible diffuse reflectance spectroscopy (UV/vis DRS) revealed a broad absorption band with the edge at 700 nm for Ti-COF-1 (Figure 2c). The optical energy gap (E_{a}) of **Ti-COF-1** was estimated to be 1.86 eV by the Tauc plot (Figure S11).^[12] The highest occupied molecular orbital (HOMO) energy level of Ti-COF-1 was measured to be 1.92 eV via VB X-ray photoelectron spectroscopy (XPS). The lowest unoccupied molecular orbital (LUMO) energy level was calculated to be 0.06 eV according to the equation E_{LUMO} = $E_{\rm HOMO} - E_{\rm g}$. It is worth noting that the low $E_{\rm g}$ of **Ti-COF-1** can enhance visible light harvesting and improve its photocatalytic activity. Moreover, **Ti-COF-1** was found to exhibit high thermal stability with a 60% retention of its initial mass at 800 °C as demonstrated by the thermogravimetric analysis (TGA) (Figure S12). After submersion in NaOH (6 M) solutions, HCI (6 M) solutions, or different organic solvents for 3 d, all the characteristic FT-IR signals of **Ti-COF-1** remained, confirming its good chemical stability (Figure S13).



Figure 1. (a) Synthesis of Na₂Ti(2,3-DHTA)₃. (b) X-ray single crystal structure of Na₂Ti(2,3-DHTA)₃. All H atoms, Na⁺ and solvent molecules have been omitted for clarity (C: grey; O: red; Ti: yellow). (c) Synthesis of **Ti-COF-1**.



Figure 2. (a) The FT-IR spectra of PyTTA, Na₂Ti(2,3-DHTA)₃ and Ti-COF-1. (b) The ¹³C CP/MAS NMR spectrum of Ti-COF-1. (c) The UV/vis DRS of Ti-COF-1. (d) The experimental PXRD pattern (red), Pawley refined pattern (black), and calculated pattern (blue) of Ti-COF-1, and their differences (green). (e) The N₂ adsorption/desorption isotherms and (f) pore distribution of Ti-COF-1.

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Figure 3. (a) The structure of Ti-COF-1 with soc topology. (b) Ti₈ cubic cage decorated with 24 linking groups in Ti-COF-1. (c) Each of the four Ti₈ cubic cages is surrounded by vertically-crossed channels with a size of 16 Å. (d) The channels are interconnected to further form 3D gridding channels. (e) The " $3 \times 3 \times 3$ " 3D cavity view of Ti-COF-1 with soc topology. The embedded cavities and 3D channels are represented by yellow balls and blue polyhedrons, respectively. (f) The model structure of Ti-COF-1. The 2D grids with different orientation are represented by different colors.

The powder X-ray diffraction (PXRD) pattern of Ti-COF-1 revealed diffraction peaks at 3.8°, 5.4°, 6.5°, and 7.7°, which respectively correspond to the (011), (200), (112) and (202) facets. The experimental PXRD pattern agrees well with the theoretical simulation (Figure 2d). It is proposed that Ti-COF-1 adopts the I_{23} space group (a = b = c = 32.59 Å, $\alpha = \beta = \gamma = 90^{\circ}$, R_{wp} = 7.17 % and R_p = 6.35 %). On the basis of the Ti(IV) octahedral complex $Ti(2,3-DHTA)_3^{2-}$ with six aldehyde grous acting as the 6-connected nodes and the square organic ligand PyTTA acting as the 4-connected building units, the topological analysis reveals that Ti-COF-1 has an edge-transitive (6, 4)connected net with a soc topology (Figure 3a). Ti-COF-1 presents an anionic framework with Na⁺ as the counterions. As shown in Figure 3b, Ti(IV) ions occupy the eight vertices, while planar PyTTA units make up the six faces, forming a cubic titanium-organic cage with a cavity diameter of 14 Å. The vertices of each Ti₈ cubic cage are decorated with 24 linking groups. In Ti-COF-1, every four cages are spaced by two perpendicular channels (Figure 3c), and each cage is surrounded by connected channels (Figure 3d). As revealed by the 3D view (Figure 3e), channels of 16 \times 16 Å² are interconnected vertically to form a 3D configuration. From another point of view, Ti-COF-1 can be considered as an interlocking 3D framework structure (Figure 3f). 2,3-DHTA can be connected with planar PyTTA units to form 2D square grids, and the coordination effect of Ti(IV) metals drive these 2D square grids to be vertically intersected and mechanically

interlocked, forming the 3D framework (Figure S14). To the best of our knowledge, **Ti-COF-1** represents the first example of 3D MCOFs with a **soc** topology.

The N₂ adsorption/desorption isotherms of **Ti-COF-1** exhibited a standard type-I curve with a rapid N₂ uptake at relatively low pressures ($P/P_0 < 0.1$), which are the characteristics of microporous frameworks.^[13] Its Brunauer–Emmett–Teller (BET) specific surface area was calculated to be 1000.4 m² g⁻¹ (Figure 2e). The pore size was calculated to be about 1.55 nm by non-local density functional theory, which is consistent with the theoretical pore diameter of 1.6 nm (Figure 2f).

Scanning electron microscopy (SEM) showed that **Ti-COF-1** existed in the form of distorted cubes (Figure S15a), the size of which is approximately 200 nm (Figure S15b). High-resolution transmission electron microscopy (HRTEM) confirmed the cubic morphology (Figure S15c). The high-resolution lattice fringes revealed the high crystallinity of **Ti-COF-1** (Figure S15d and S15e). The symmetrically rectangularly alligned diffraction spots as shown by the Fourier-filtered image (inset in Figure S15e) indicate the highly ordered structure of **Ti-COF-1**. Moreover, the dislocation diagram obtained by inverse Fourier transform indicated quadrilateral gridding frameworks, which is consistent with the **soc** structure (Figure S15f). Observation from the (200) direction (Figure S15d-e) revealed distinct 1D channels with a uniform diameter of 1.6 nm, which is consistent with the theoretical pore diameter of 16 Å. The EDS mapping images

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revealled and confirmed the uniform distribution of the C, N, O and Ti elements in **Ti-COF-1** (Figure S15g).

Table 1. Photocatalytic Meerwein addition reactions by Ti-COF-1^[a]



[a] Reaction conditions: catalyst **Ti-COF-1** (10 mg, 0.37 mol % based on unit cell), the arenediazonium salt (1 equiv, 0.25 mmol), alkene (2 equiv), and water (1 equiv) were dissolved with 1 mL of CH₃CN in a 10 mL snap vial equipped with magnetic stirring bar at room temperature under a 27 W white LED irradiation for 24 h. [b] Isolated yield. [c] TON is defined as the total moles of product formed (n_{prod}) divided by total moles of **Ti-COF-1** catalyst unit cell^[14] (n_{cat}). TON = n_{prod} / n_{cat}.

It is thus concluded that **Ti-COF-1** possesses high porosity, high crystallinity, superior stability, and appropriate HOMO and LUMO energy levels. These characteristics meet the basic criteria of a heterogeneous photocatalyst. Meerwein addition reaction is a valuable synthetic method for aryl radical chemistry and has been used in industrial processes for the synthesis of drugs and fine chemicals.^[15] Therefore, the photocatalytic Meerwein addition reaction to demonstrate the photocatalytic activity of **Ti-COF-1** (see SI).

As can been seen in Table 1, the **Ti-COF-1**-catalyzed Meerwein addition reactions were found to tolerate various arenediazonium salts and alkenes to afford desired products in 49-75 % yields with 132-202 turnover number (TON). In detail, styrene with halide functional groups, such as -F and -Cl at the para position produced the product with good yields (Table 1, entries 2 and 3). Arenediazonium salts bearing electron-

withdrawing and electron-donating substituents including nitro, ester and methoxyl groups, afforded the products with moderate to good yields (Table 1, entries 1, 3, 4, 5 and 6). In addition, The reaction cannot be carried out without light or a photocatalyst (Table S1, entries 7 and 8), and low yield was obtained when Na₂Ti(2,3-DHTA)₃ precursor was used instead of **Ti-COF-1** (Table S1, entries 9 and 10). Compared to the other catalysts (Table S2), **Ti-COF-1** is an efficient heterogeneous catalyst for photocatalytic Meerwein addition reactions. Moreover, **Ti-COF-1** can be readily recycled, and its catalytic activity showed only slight change after 5 runs (Figure S18a). Further, it was found that the crystallinity of the recycled **Ti-COF-1** was well maintained (Figure S18b).



Figure 4. Proposed mechanism for the photocatalytic Meerwein addition reactions on Ti-COF-1.

Based on the previous studies,^[16] and our experimental results, a possible mechanism for Ti-COF-1 to catalyze Meerwein addition reactions is proposed (Figure 4). The porous structure and anionic skeleton make Ti-COF-1 an excellent adsorbent for cationic arenediazonium salts, which is favorable for photocatalytic reactions. The coordination between catechol and metal ions synergistically improve ligands the photocatalytic properties.^[17] electrochemical and Upon irradiation, Ti(IV) coordinated active centers can efficiently enhance the charge mobility, thereby exciting Ti-COF-1 to produce electrons and holes. The adsorbed arenediazonium salt 1 is reduced by the photo-excited electrons to form aryl radical 4. The subsequent addition reaction of the aryl radical to styrene 2 delivers the radical intermediate 5, which is oxidized by the hole of Ti-COF-1 to form a cation 6. Finally, the intermediate 6 is attacked by CH₃CN to produce another intermediate 7, followed by its hydrolysis to produce the amide product 3.

In conclusion, the "MOC-to-MCOF" strategy was proven to be an efficient method that produces 3D anionic COFs with **soc** topology using octahedral Ti(IV) complex as the building unit. **Ti-COF-1** contains interconnected channels for high specific surface area, possesses fast charge mobility, and exhibits COMMUNICATION

promising photocatalytic activity for Meerwein addition reactions. This research can be extended to enrich the structure and functionality of 3D frameworks, and will inspire intense research on MCOFs.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (22075108, 21771089, 21905116), the Natural Science Foundation of Jiangsu Province (BK20190614), and MOE & SAFEA for the 111 Project (B13025).

Keywords: covalent organic framework • three-dimensional • topology • Ti(IV) complex • photocatalytic reactions

- a) A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science* 2005, *310*, 1166-1170; b) H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortes, A. P. Côté, R. E. Taylor, M. O'Keeffe, O. M. Yaghi, *Science* 2007, *316*, 268-272; c) N. Huang, P. Wang, D. Jiang, *Nat. Rev. Mater.* 2016, *1*, 16068; d) C. S. Diercks and O. M. Yaghi, *Science* 2017, *355*, eaal1585.
- [2] a) D. Rodríguez-San-Miguel, F. Zamora, *Chem. Soc. Rev.* 2019, *48*, 4375-4386; b) X. Guan, F. Chen, Q. Fang and S. Qiu, *Chem. Soc. Rev.* 2020, *49*, 1357-1384; c) Z. Li, T. He, Y. Gong, D. Jiang, *Acc. Chem. Res.* 2020, *53*, 1672-1685; d) K. Geng, T. He, R. Liu, S. Dalapati, K. T. Tan, Z. Li, S. Tao, Y. Gong, Q. Jiang, D. Jiang, *Chem. Rev.* 2020, *120*, 8814-8933.
- [3] a) X. Liu, D. Huang, C. Lai, G. Zeng, L. Qin, H. Wang, H. Yi, B. Li, S. Liu, M. Zhang, R. Deng, Y. Fu, L. Li, W. Xue, S. Chen, *Chem. Soc. Rev.* 2019, *48*, 5266-5302; b) Z. Wang, S. Zhang, Y. Chen, Z. Zhang, S. Ma, *Chem. Soc. Rev.* 2020, *49*, 708-735; c) W. K. Haug, E. M. Moscarello, E. R. Wolfson, P. L. McGrier, *Chem. Soc. Rev.* 2020, *49*, 839-864; d) H. Wang, H. Wang, Z. Wang, L. Tang, G. Zeng, P. Xu, M. Chen, T. Xiong, C. Zhou, X. Li, D. Huang, Y. Zhu, Z. Wang, J. Tang, *Chem. Soc. Rev.* 2020, *49*, 4135-4165.
- [4] a) Y. Jin, Y. Hu, W. Zhang, *Nat. Rev. Chem.* 2017, *1*, 0056; b) D.
 Rodríguez-San-Miguel, C. Montoro, F. Zamora, *Chem. Soc. Rev.* 2020, *49*, 2291-2302; c) S. B. Alahakoon, S. D. Diwakara, C. M. Thompson, R.
 A. Smaldone, *Chem. Soc. Rev.* 2020, *49*, 1344-1356; d) R.-R. Liang, S.-Y. Jiang, R.-H. A, X. Zhao, *Chem. Soc. Rev.* 2020, *49*, 3920-3951.
- [5] a) G. Lin, H. Ding, D. Yuan, B. Shan, C. Wang, J. Am. Chem. Soc. 2016, 138, 3302-3305; b) H. Ding, J. Li, G. Xie, G. Lin, R. Chen, Z. Peng, C. Yang, B. Wang, J. Sun, C. Wang, Nat. Commun. 2018, 9, 5234; c) C. Gao, J. Li, S. Yin, G. Lin, T. Ma, Y. Meng, J. Sun, C. Wang, Angew. Chem., Int. Ed. 2019, 58, 9770-9775; d) C. Gao, J. Li, S. Yin, J. Sun, C. Wang, J. Am. Chem. Soc. 2020, 142, 3718-3723; e) H. Li, J. Ding, X. Guan, F. Chen, C. Li, L. Zhu, M. Xue, D. Yuan, V. Valtchev, Y. Yan, S. Qiu, Q. Fang, J. Am. Chem. Soc. 2020, 142, 13334-13338; f) C. Gropp, T. Ma, N. Hanikel, O. M. Yaghi, Science 2020, 370, eabd6406; g) X. Kang, X. Han, C. Yuan, C. Cheng, Y. Liu, Y. Cui, J. Am. Chem. Soc. 2020, 142, 16346-16356.
- [6] J. Q. Dong, X. Han, Y. Liu, H. Y. Li, Y. Cui, Angew. Chem. Int. Ed. 2020, 59, 13722-13733.
- a) Y. Z. Liu, Y. H. Ma, Y. B. Zhao, X. X. Sun, F. Gandara, H. Furukawa,
 Z. Liu, H. Y. Zhu, C. H. Zhu, K. Suenaga, P. Oleynikov, A. S. Alshammari, X. Zhang, O. Terasaki, O. M. Yaghi, *Science* 2016, *351*, 365-369; b) Y. Zhao, L. Guo, F. Gandara, Y. Ma, Z. Liu, C. Zhu, H. Lyu,
 C. A. Trickett, E. A. Kapustin, O. Terasaki, O. M. Yaghi, *J. Am. Chem. Soc.* 2017, 139, 13166-13172; c) Y. Liu, Y. Ma, J. Yang, C. S. Diercks,
 N. Tamura, F. Jin, O. M. Yaghi, *J. Am. Chem. Soc.* 2018, *140*, 16015-16019; d) Y. Liu, C. S. Diercks, Y. Ma, H. Lyu, C. Zhu, S. A. Alshmirri,
 S. Alshihri, O. M. Yaghi, *J. Am. Chem. Soc.* 2019, *141*, 677-683.
- [8] a) D. W. Zhang, T. K. Ronson, J. R. Nitschke, *Acc. Chem. Res.* 2018, 51, 2423-2436; b) E. G. Percástegui, T. K. Ronson, J. R. Nitschke, *Chem. Rev.* 2020, 120, 13480-13544.

- [9] J. Mosquera, B. Szyszko, S. Ho, J. R. Nitschke, *Nat Commun.* 2017, 8, 14882.
- [10] C. M. Hong, R. G. Bergman, K. N. Raymond, F. D. Tloste, Acc. Chem. Res. 2018, 51, 2447-2455.
- [11] CCDC 2056407 of Na₂Ti(2,3-DHTA)₃ contains the supplementary crystallographic data for this paper. These data are available free of charge from the Cambridge Crystallographic Data Centre.
- [12] J. Tauc, Mater. Res. Bull. 1968, 3, 37-46.
- [13] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, *Pure Appl. Chem.* 2015, 87, 1051.
- [14] S. Lin, C. S. Diercks, Y. B. Zhang, N. Kornienko, E. M. Nichols, Y. Zhao, A. R. Paris, D. Kim, P. Yang, O. M. Yaghi, C. J. Chang, *Science*, **2015**, 349, 1208-1212.
- [15] a) M. K. Staples, R. L. Grange, J. A. Angus, J. Ziogas, N. P. H. Tan, M. K. Taylor, C. H. Schiesser, *Org. Biomol. Chem.* 2011, 9, 473-479; b) G. Pratsch, C. A. Anger, K. Ritter, M. R. Heinrich, *Chem. Eur. J.* 2011, *17*, 4104-4108; c) M. R. Heinrich, *Chem. Eur. J.* 2009, *15*, 820-833; d) N. Zhu, T. Wang, L. Ge, Y. Li, X. Zhang, H. Bao, *Org. Lett.* 2017, *19*, 4718–4721.
- [16] D. Prasad Hari, T. Hering, B. König, Angew. Chem. Int. Ed. 2014, 53, 725-728.
- [17] Y. Yan, C. Li, Y. Wu, J. Gao, Q. Zhang, J. Mater. Chem. A. 2020, 8, 15245-15270.

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