A semiconductive and microporous one-dimensional tubular metal-organic framework

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ABSTRACT: We report the first one-dimensional tubular metal-organic framework (MOF) [Ni(Cu-H_6TPPA)]·2DMA (H_8TPPA = 5,10,15,20-tetrakis[*p*-phenylphosphonic acid] porphyrin) in the literature. The structure of this MOF, known as GTUB4, was solved using single crystal X-ray diffraction and its surface area was calculated to be 1102 m^2/g, making it the phosphonate MOF with the highest reported surface area. GTUB4 also possesses a narrow indirect band gap of 1.9 eV and a direct band gap of 2.16 eV, making it a semiconducting MOF. Thermogravimetric analysis of GTUB4 suggests that it is thermally stable up to 400°C. Owing to its high surface area, low band gap, and thermal stability, GTUB4 could find applications as electrodes in supercapacitors.

Metal organic frameworks (MOFs) are microporous materials that contain well-defined micropores composed of organic and inorganic surfaces. [1-6] They have been used in applications ranging from gas absorption, sequestration of greenhouse gases [7,8], catalysis [9, 10] magnetism [11-14], drug delivery [15, 16], cosmetic applications [17], food packaging and transportation [18, 19], proton conductive membranes [20, 21] and electrical conduction [22-24]. Although thousands of MOFs have been reported in the literature, the structural diversity of MOFs, MOF linker core geometries, and different metal-binding functional groups have not been fully exploited yet. Recently, two new families of MOFs have emerged, which employ phosphonic and phosphinic acids as metal-binding units, in contrast with the conventional MOFs that contain carboxylates and azolates. [25-28] Phosphonic acids are able to support extremely rich metal-binding modes, while phosphinic acids have carboxylate-like metal-binding modes. [28] The presence of d-orbitals in the phosphorus atom can give rise to rich electronic interactions, which have resulted in completely different geometries compared to those of conventional MOFs. [25-28] Owing to the higher strength of the C-P and P-O bonds compared to R-C=O bonds, phosphonate MOFs exhibit higher thermal and chemical stabilities compared to conventional MOFs. [12, 29, 30] To the best of our knowledge, the total number of microporous phosphonate MOFs is currently less than 0.001% of the total number of reported MOFs. Nevertheless, they have already opened new vistas in catalysis, [30, 31] proton conductivity, [20, 32, 33] and biological applications [34].

One of the often unexplored properties in MOF research is semiconductivity. [22-24] Traditional carboxylate MOFs are generally known to be insulators. The majority of the known semiconductive MOFs are based on ortho-diimine, ortho-dihydroxy, and azolate linkers; however, due to their very conservative metal-binding units, further structural development has been limited. [1, 22-24] Therefore, new metal-binding units that give rise to high structural diversity and semiconductivity are needed. In this direction, the phosphonic acid metal-binding unit (R-PO_3^{2-}) – containing phosphorus, which is a good conductor and has a negative charge that is evenly distributed over the three tetrahedronally oriented oxygen atoms – has shown great promise. We have recently shown that the presence of the phosphorus d-orbitals in phosphonic acids promotes electron delocalization in the one-dimensional inorganic building unit (IBU) of the phosphonate MOF TUB75, which is composed of polyaromatic 1,4-naphthalenediphosphonic acid linkers and one-dimensional copper-containing IBUs and has a narrow band gap of 1.4 eV. [13] To build upon this work, in this study, we used a conjugated tetratopic linker, H_8-TPPA, to synthesize another semiconductive phosphonate MOF, namely [Ni(Cu-H_4TPPA)]·2DMA (**GTUB-4**), which has a unique one-dimensional microporous tubular structure with a very high BET surface area of 1102 m^2/g and a narrow indirect band gap of 1.90 eV.

Due to the rich metal-binding modes of organophosphonates, the rational synthesis of phosphonate MOFs into predefined one-, two-, and three-dimensional frameworks has been a great challenge. [25-27] Previously, phosphonate monoesters mimicking the carboxylate metal binding were used to generate microporous MOFs. [35, 36] Recently, we developed a new strategy to retain mono-deprotonated R-PO_3H^{-1} in hydrothermal reactions via a pH-controlled synthesis. [37, 38] The R-PO_3H^{-1} metal-binding unit also provides carboxylate-like metal binding to generate predictable phosphonate MOFs. In this study, we aimed to attain the simplest metal-binding modes with the tetratopic, structurally rigid, and planar phosphonic acid H_8TPPA (which contains a conjugated porphyrin core), whose phosphonic acid moieties are separated by ca. 90° from one other. Thus, when H_8TPPA is coordinated to molecular IBUs in the simplest 1.100 mode (in Harris notation [39]), they are expected to create square or rectangular void spaces. In this connection, our goal was to create H_4TPPA^{4-} (in which each phosphonate arm is mono-deprotonated) to achieve the 1.100 metal-binding mode. In addition, we aimed to create an extended one-dimensional conjugated system that supports semiconductivity. To achieve this, we performed a low-temperature synthesis in DMF to promote the formation of molecular IBUs, as a high-temperature hydrothermal synthesis could provide enough energy to form one-dimensional or two-dimensional IBUs. Furthermore, in a square planar coordination environment, the high energy d^9 electrons of Cu(II) can support conductive behavior in MOFs. [22] Inside a porphyrin core, Cu(II) usually adopts a square planar coordination environment. Therefore, we adapted the Pd-catalyzed Arbuzov reaction to synthesize metal-free H_8-TPPA. Due to the large ionic radius of the Pd atom, it does not readily incorporate into the porphyrin ring, allowing one to incorporate other metal atoms into the porphyrin core. [34, 40] Later, we introduced square planar Cu(II) into H_8-TPPA's imidazole ring to synthesize Cu-H_8TPPA (the deprotonated imidazole hydrogens are omitted in this formula). **GTUB-4** was synthesized in a DMF/H_2O and phenylphosphonic acid (modulator) mixture at 80 °C for 24 h, giving rise to long purple needle crystals in high yield (see SI for experimental details). These carefully controlled conditions were required to achieve the simplest 1.100 phosphonate metal-binding modes.

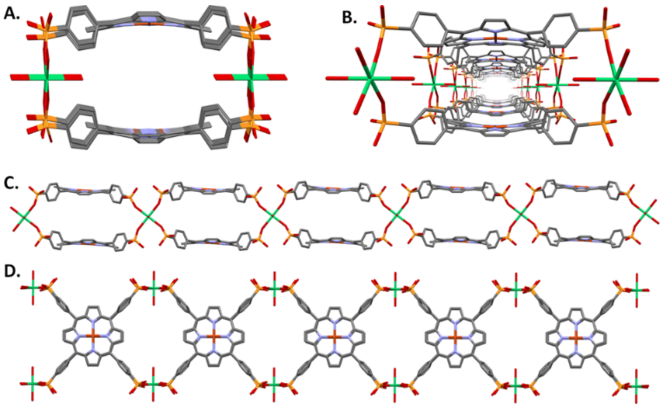

Figure 1. a) Edge view of the rectangular void channel of GTUB-4. b) Perspective view of the rectangular void channel. c) Side-top view of tubular structure and its hexagonal sieves. d) Another side view of **GTUB-4** facing the CuH_4TPPA^{4-} building unit with square void channels.

The structure of **GTUB-4** was solved using X-ray crystallography. As seen in Figure 1, **GTUB-4** has a one-dimensional tubular structure, which is the first of its kind among the MOFs reported to date. **GTUB-4** has one rectangular void channel extending through the tube (see Figures 1a and 1b) and two different hexagonal voids on the sides, top, and bottom of the tube (see Figures 1c and 1d). The phosphonate metal-binding groups in **GTUB-4** have 1.100 metal-binding modes corresponding to the simplest type of metal-binding mode. As mentioned earlier, this was achieved under well-controlled pH, temperature, and solvent conditions – the three variables that control the structural diversity of phosphonate MOFs. The crystal structure of **GTUB-4** reveals that it contains one of the simplest IBUs, namely octahedral nickel metal centers coordinated to the four phosphonic acid metal-binding groups of H_8-TPPA. As seen in Figures 1A and 1B, the basal plane of octahedral Ni exclusively connects the Cu-H_4TPPA^{4-} linkers, while the apical positions of Ni are occupied by two water molecules. In the crystal structure, the MOF tubes are packed at 41.87° with respect to each other, leading to growth in two different directions (see Figure 2D). As the tubular structure of **GTUB-4** is composed of three distinct pore sites (see Figures 1A, 1C, and 1D), the textural properties of **GTUB-4** were characterized with molecular simulations (see SI for details). **GTUB-4** was computed to have a specific pore volume of 0.425 cm^3/g, an accessible surface area of 1102 m^2/g, and pores of approximately 5 Å in diameter (Figure S7).

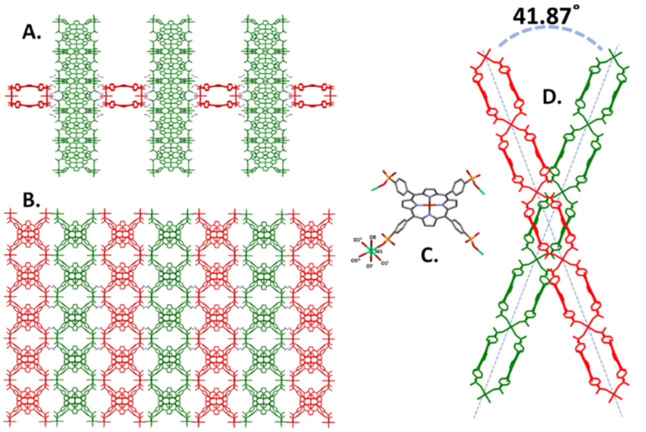

Figure 2. a) b) and d) contain different views of the cross-packed **GTUB-4** tubes in the crystal lattice. c) Cu-H_4TPPA^{4-} metal-binding modes with Ni.

The structure of **GTUB-4** shown in Figure 1D suggests that H_8TPPA's conjugation extends over the mono-deprotonated tetrahedral phosphonate metal-binding unit R-P=O(OH)O^{-1}, in which the phosphonate electrons could delocalize over the tetrahedral geometry. In light of these results, we used solid-state diffuse reflectance spectroscopy (DRS) to determine the optical band gap of **GTUB-4** to see whether it is semiconducting or not (see Figure 3). The indirect optical band gap of **GTUB-4** was found to be 1.9 eV (see SI for calculation details). The narrowness of the band gap is presumably due to the extension of conjugation via the mono-deprotonated phosphonate metal-binding unit.

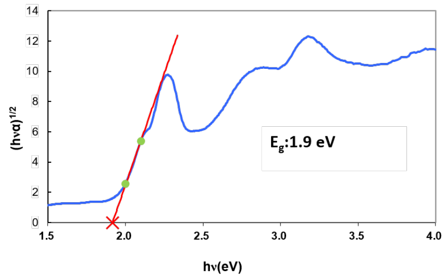

Figure 3. Estimation of the indirect band gap of **GTUB-4** via Tauc plotting of the DRS spectrum.

The presence of metal ions could increase the thermal stability of MOFs compared to that of the linkers due to the presence of additional covalent and ionic bonding opportunities in MOFs. Thus, we studied the thermal behaviors of H_8-TPPA, Cu-H_8TPPA, [Ni(Cu-H_4TPPA)]·2DMA, **(GTUB-4)** via thermogravimetric analysis (TGA). As seen in Figure S3, the TGA curve obtained from the hand-picked **GTUB-4** crystals indicates that the solvent and water molecules evaporate from **GTUB-4** until 100 °C. The second step of ~11.1% weight loss corresponds to the evaporation of dimethylammonium cations in the crystal lattice (12.3% calculated). The third step of ~28.8 % weight loss between ~400 °C and ~650 °C corresponds to nearly half of the organic components of H_8TPPA (52% calculated). The decomposition of **GTUB-4** continues above 900°C, suggesting that **GTUB-4** might be converted into thermally stable phosphides above 650°C. [44]

Herein, we reported on the first tubular MOF, **GTUB-4**, which was constructed using the highly conjugated H_8-TPPA linker. The strict pH and temperature control enabled the formation of a one-dimensional tubular structure with a calculated surface area of 1102 m^2/g. The conjugated porphyrin core and electron delocalization around the phosphonate metal-binding unit are believed to enhance the conjugation along the 1D structure. This results in a narrow band gap of 1.9 eV, indicating that **GTUB-**4 is a semiconductor. We were selectively able to introduce square planar Cu(II) with high energy electrons into the porphyrin core of **GTUB-4**, where the linker connectivity is achieved via octahedral Ni centers. The thermal decomposition pattern of **GTUB-4** indicates that it is thermally stable up to 400 °C, after which the organic components of the porphyrin core collapse. The presence of water at the apical position of the octahedral Ni site suggests the possibility of post-synthetic modifications of **GTUB-4**. We are currently working on combining the one-dimensional tubular channels to synthesize a three-dimensional version of **GTUB-4**.

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Author Contributions

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ABBREVIATIONS

MOF – metal-organic framework
IBU – inorganic building unit

REFERENCES

1. Li, H.; Eddaoudi, E.; O'Keeffe, M.; Yaghi, O. M., Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* 1999, 402, 276-279.
2. Schneemann, A.; Bon, V.; Schwedler, I.; Senkovska, I.; Kaskel, S.; Fischer, R. A., Flexible metal–organic frameworks. *Chem. Soc. Rev.* 2014, 43, 6062-6096.
3. Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange F., Crystallized frameworks with giant pores: Are there limits to the possible?. *Acc. Chem. Res.* **2005**, 38, 4, 217-225.
4. Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M. The chemistry and applications of metal-organic frameworks. *Science*. 2013, 341, 974.
5. Zhou, H. C.; Long, J. R.; Yaghi, O. M. Introduction to metal–organic frameworks. *Chem. Rev.* 2012, **112**, 673-674.
6. Stock, N.; Biswas, S. Synthesis of metal-organic frameworks (MOFs): Routes to various MOF topologies, morphologies, and composites. *Chem. Rev.* 2012, **112**, 2, 933-969.
7. Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J., Reticular synthesis and the design of new materials. *Nature* **2003**, 423, 705-714.
8. Hanikel, N.; Prévot, M. S.; Fathieh, F.; Kapustin, E. A.; Lyu, H.; Wang, H.; Diercks, N. J.; Glover, T. G.; Yaghi, O. M., Rapid cycling and exceptional yield in a metal-organic framework water harvester. *ACS Cent. Sci.*, **2019**, 5, 1699-1706.
9. Dhakshinamoorthy, A.; Li, Z.; Garcia, H. Catalysis and photocatalysis by metal organic frameworks. *Chem. Soc. Rev.* **2018**, 47, 8134-8172.
10. Yang, D.; Gates, B. C., Catalysis by metal-organic frameworks: perspective and suggestions for future research. *ACS Catal.* **2019**, 9, 3, 1779-1798.
11. Espallargas, G. M.; Coronado, E., Magnetic functionalities in MOFs: From the framework to the pore. *Chem. Soc. Rev.* 2018, **47**, 533-557.
12. Zorlu, Y.; Erbahar, D.; Çetinkaya, A.; Bulut, A.; Erkal, T. S.; Yazaydin, A. O.; Beckmann, J.; Yücesan, G., A cobalt arylphosphonate MOF-superior stability, sorption and magnetism. *Chem. Commun.* **2019**, 55, 3053-3056.
13. Siemensmeyer, K.; Peeples, C. A.; Tholen, P.; Çoşut, B.; Hanna, G.; Yücesan, G. Phosphonate Metal-Organic Frameworks: A Novel Family of Semiconductors. *ChemRxiv*. **2020**, Preprint. https://doi.org/10.26434/chemrxiv.11671806.v1
14. Yang, C.; Dong, R.; Wang, M.; Petkov, P. S.; Zhang, Z.; Wang, M.; Han, P.; Ballabio, M.; Bräuninger, S. A.; Liao, Z.; Zhang, J.; Schwotzer, F.; Zschech, E.; Klauss, H. H.; Cánovas, E.; Kaskel, S.; Bonn, M.; Zhou, S.; Heine, T.; Feng, X., A semiconducting layered metal-organic framework magnet. *Nat. Commun.* **2019**, 10, 1-9.
15. Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C., Metal-organic frameworks in biomedicine. *Chem. Rev.* **2012**, 112, 1232-1268.
16. Hartlieb, K. J.; Ferris, D. P.; Holcroft, J. M.; Kandela I.; Stern, C. L.; Nassar, M. S.; Youssry, Y.; Botros J.; Stoddart, J. F., Encapsulation of Ibuprofen in CD-MOF and Related Bioavailability Studies. *Mol. Pharmaceutics,* **2017**, 145, 1831-1839.
17. Hartlieb, K. J.; Peters, A. W.; Wang, T. C.; Deria, P.; Farha, O. K.; Hupp, J. T.; Stoddart, J. F., Functionalised cyclodextrin-based metal–organic frameworks. *Chem. Commun.*, **2017**, 53, 7561-7564.
18. Wang, P. L.; Xie, L. H.; Joseph, E. A.; Li, J. R.; Su, X. O.; Zhou, H. C., Metal–organic frameworks for food safety. *Chem. Rev.* **2019**, 119, 18, 10638-10690.
19. Zhang, B.; Luo, Y.; Kanyuck, K.; Bauchan, G.; Mowery, J.; Zavalij, P., Development of Metal-organic framework for gaseous plant hormone encapsulation to manage ripening of climacteric produce, *J. Agric. Food Chem*., **2016**, 64, 25, 5164-5170.
20. Bao, S. S.; Shimizu, G. K. H.; Zheng, L. M. Proton conductive metal phosphonate frameworks. *Coord. Chem. Rev.* **2019**, 378, 577-594.
21. Levenson, D. A.; Zhang, J.; Szell, P. M. J.; Bryce, D. L.; Gelfand, B. S.; Huynh, R. P. S. Fylstra, N.; Shimizu, G. K. H.; Effects of secondary anions on proton conduction in a flexible cationic phosphonate metal-organic framework. *Chem. Mater.* **2020**, 32, 2, 679-687.
22. Sun, L.; Campbell, M. G.; Dinca, M.; Electrically conductive porous metal–organic frameworks. *Angew. Chem. Int. Ed.,* **2016**, 55, 3566 – 3579.
23. Sheberla, D.; Bachman, J. C.; Elias, J. S.; Sun, C. J.; Shao-Horn, Y.; Dincă, M. Conductive MOF electrodes for stable supercapacitors with high areal capacitance. *Nat. Mater.* **2017**, 16, 220–224.
24. Rieth, A. J.; Tulchinsky, Y.; Dincă, M., High and reversible ammonia uptake in mesoporous azolate metal–organic frameworks with open Mn, Co, and Ni sites. *J. Am. Chem. Soc.*, **2016**, 138, 30, 9401-9404.
25. Yücesan, G.; Zorlu, Y.; Stricker, M.; Beckmann, J.; Metal-organic solids derived from arylphosphonic acids. *Coord. Chem. Rev.* **2018**, 369, 105-122.
26. Shearan, S. J.; Stock, N.; Emmerling, F.; Demel, J.; Wright, P. A. K.; Demadis, D.; Vassaki, M.; Costantino, F.; Vivani, R.;

Sallard, S.; Salcedo, I. R.; Cabeza, A.; Taddei, M., New directions in metal phosphonate and phosphinate chemistry, Crystals, **2019**, 9(5), 270.

27. Bhanja, P., Na, J.; Jing, T.; Lin, J.; Wakihara, T.; Bhaumik, A.; Yamauchi, Y., Nanoarchitectured metal phosphates and phosphonates: A new material horizon toward emerging applications, *Chem. Mater.* **2019**, 31, 15, 5343-5362.
28. Hynek J.; Brázda P.; Rohlíček J.; Londesborough, M. G. S.; Demel J., Phosphinic acid based linkers: Building blocks in metal–organic framework chemistry. *Angew. Chem.* 2018, 57, 18, 5016-5019.
29. Gagnon, K. J.; Perry, H. P.; Clearfield, A., Conventional and unconventional metal-organic frameworks based on phosphonate ligands: MOFs and UMOFs. *Chem. Rev.* **2012**, 112, 1034-1054.
30. Gao, C.; Ai, J.; Tian, H.; Wub, D.; Sun, Z., An ultrastable zirconium-phosphonate framework as bifunctional catalyst for highly active CO_2 chemical transformation. *Chem. Commun.* **2017**, 53, 1293-1296.
31. Chen, X.; Peng, Y.; Han, X., Sixteen isostructural phosphonate metal-organic frameworks with controlled Lewis acidity and chemical stability for asymmetric catalysis. *Nat. Commun.* 2017, 8, 2171
32. Gelfand, B. S.; Huynh, R. P. S.; Mah, R. K.; Shimizu, G. K. H., Mediating order and modulating porosity by controlled hydrolysis in a phosphonate monoester metal–organic framework. *Angew. Chem.* 2016, 55, 47, 14614-14617.
33. Taylor, J. M.; Mah, R. K.; Moudrakovski, I. L.; Ratcliffe, C. I.; Vaidhyanathan, R.; Shimizu, G. K. H., Facile proton conduction via ordered water molecules in a phosphonate metal-organic framework. *J. Am. Chem. Soc.* **2010**, 132, 14055-14057.
34. Maares, M.; Ayhan, M. M.; Yu, K. B.; Yazaydin, A. O.; Harmandar, K.; Haase, H.; Beckmann, J.; Zorlu, Y.; Yücesan, G.; Alkali phosphonate metal-organic frameworks. *Chem. Eur. J.* **2019**, 25, 11214-11217.
35. Iremonger, S. S.; Liang, J.; Vaidhyanathan, R.; Martens, I.; Shimizu, G. K. H.; Daff, T. D.; Aghaji, M. Z.; Yeganegi, S.; Woo, T. K. Phosphonate monoesters as carboxylate-like linkers for metal organic frameworks. *J. Am. Chem. Soc.* **2011**, 133, 50, 20048-20051.
36. Taylor, J. M.; Vaidhyanathan, R.; Iremonger, S. S.; Shimizu, G. K. H., Enhancing water stability of metal–organic frameworks via phosphonate monoester linkers. *J. Am. Chem. Soc.* **2012**, 134, 35, 14338-14340.
37. Bulut, A.; Zorlu, Y.; Wörle, M.; Çetinkaya, A.; Kurt, H.; Tam, B.; Yazaydın, A. Ö.; Beckmann, J.; Yücesan, G., Short naphthalene organophosphonate linkers to microporous frameworks. Chem. Select. **2017**, 2, 7050-7053.
38. Bulut, A.; Zorlu, Y.; Kirpi, E.; Çetinkaya, A.; Wörle, M.; Beckmann, J.; Yücesan, G., Synthesis of Cu(II)-organophosphonate framework with predefined void spaces. *Cryst. Growth Des.* **2015**, 15, 5665−5669.
39. Coxall, R. A.; Harris, S. G.; Henderson, D. K.; Parsons, S.; Tasker, P. A.; Winpenny, R. E. P., Inter-ligand reactions: in situ formation of new polydentate ligands. *Dalton Trans.* **2000**, 14, 2349.
40. Yucesan, G.; Golub, V.; O'Connor, C. J.; Zubieta, J.; Organic/inorganic hybrid frameworks constructed from tetrapyridylporphyrin and vanadium oxide chains. *CrystEngComm*, **2004**, 6, 323.
41. Tauc, J.; Grigorovici, R.; Vancu, A.; Optical Properties and Electronic Structure of Amorphous Germanium. *Phys. Status Solidi*, **1966**, 15, 627-637.
42. Tauc, J.; Optical Properties of Solids, Abeles, North Holland, Amsterdam, **1972**.
43. Davis, E. A.; Mott, N. F.; Conduction in non-crystalline systems V. Conductivity, optical absorption and photoconductivity in amorphous semiconductors. *Philos. Mag*., **1970,** 22, 903-922.
44. Zhang, R.; Russo, P. A.; Feist, M.; Amsalem, P.; Koch, N., Pinna, N., Synthesis of nickel phosphide electrocatalysts from hybrid metal phosphonates. *ACS Appl. Mater. Interfaces* **2017**, 9, 16, 14013-14022.