

Tertiary Building Units: Synthesis, Structure, and Porosity of a Metal–Organic Dendrimer Framework (MODF-1)[‡]

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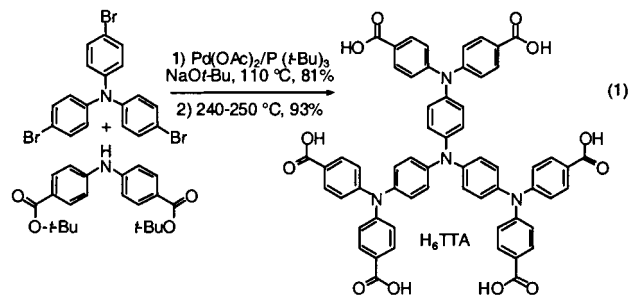
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Studies on the assembly of metal–organic frameworks (MOFs) have uncovered methods to build extended structures from molecular building blocks.^{1–3} The synthesis of a new type of porous material using strategies based on the expansion and decoration of vertexes in basic nets has demonstrated the wide scope of this chemistry.⁴ In particular, crystalline MOFs that maintain their open structure in the absence of guests can perform highly selective separations.⁵

Most MOFs have been constructed from simple unbranched connectors, such as 1,4-benzenedicarboxylate and 1,3,5-benzenetricarboxylate.^{4a} In contrast, branched connectors, such as small dendrimers, have not been used to prepare MOFs because these connectors are more flexible. This flexibility could impede crystallization and characterization by single-crystal X-ray diffraction.⁶ Yet, crystalline metal–organic dendrimer frameworks (MODFs) generated from branched linkers such as small dendrimers would (a) provide information on dendrimer structure and (b) allow construction, from nanometer-sized building blocks, of well-defined frameworks with chemical and physical properties derived from those of the organic units. We report the synthesis, crystal structure, and sorption chemistry of the first MODF:

Zn₄O(TTA)(DMA)₂·(DMA)₃(H₂O)₂₁ (DMA = *N,N*-dimethylacetamide), which contains zinc ions linking a carboxy-terminated triarylamine dendrimer 4,4',4''-tris(*N,N*-bis(4-carboxylphenyl)-amino)triphenylamine (H₆TTA).

The carboxy-terminated, first-generation dendrimer with triarylamine branches and a triarylamine core was prepared (eq 1) using recently developed palladium-catalyzed amination methodology, which provides rapid access to a variety of triarylamine materials.⁷ We prepared the H₆TTA linker containing six peripheral carboxyl groups to coordinate metal ions by coupling of 4,4',4''-tribromotriphenylamine with 4,4'-di-*tert*-butylcarboxy diphenylamine and subsequent thermal conversion of the *tert*-butyl carboxylates to the free acids.



To prepare MODF-1, H₆TTA (0.002 g, 2.0 × 10⁻⁶ mol) and Zn(NO₃)₂·6H₂O (0.012 g, 4.0 × 10⁻⁵ mol) were dissolved in a mixture of DMA/EtOH/H₂O (1.5/0.4/0.1 mL), and the resulting solution was placed in a quartz tube (10 mm × 8 mm o.d. × i.d., 140 mm length). The sample was heated at a constant rate of 0.1 °C/min to 75 °C, held at 75 °C for 24 h, cooled at a constant rate of 0.1 °C/min to 65 °C, held at this temperature for 10 h, and cooled to room temperature. Light-green crystals of MODF-1 were formed and isolated by washing with a mixture of DMA and EtOH (3 × 4 mL) and drying briefly in air (ca. 1 min) (0.002 g, 56%). The infrared spectrum of this compound showed that the carboxylic acid units had been deprotonated as indicated by absence of ν_{O–H} stretch and a shifted of ν_{C=O} stretch from 1690.4 cm⁻¹ in the free carboxylic acid to 1599.0 cm⁻¹ in MODF-1, as for other Zn-bound carboxylates.⁸ The structure was deduced from chemical microanalysis and single-crystal X-ray diffraction data.^{9,10}

(6) To our knowledge no crystalline network materials built from organic dendrimers have been reported. For structures of discrete organometallic dendrimers, see: (a) Kriesel, J. W.; König, S.; Freitas, M. A.; Marshall, A. G.; Leary, J. A.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 12207–12215. (b) Lambert, J. B.; Hongwei, W. *Organometallics* **1998**, *17*, 4904–4909. (c) Mekelburger, H.-B.; Rissanen, K.; Vogtle, F. *Chem. Ber.* **1993**, *126*, 1161–1169. For references and reviews on organometallic dendrimers, see: (d) Knapen, J. W. J.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659. (e) Onitsuka, K.; Takahashi, S. *J. Synth. Org. Chem. Jpn.* **2000**, *58*, 988. (f) Brunner, H. *J. Organomet. Chem.* **1995**, *500*, 39.

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(9) The preparation is fully reproducible for MODF-1 and for other MODFs derivatives employing Cu (II), which we are currently studying. Elemental microanalysis for Zn₄O(TTA)(DMA)₂·(DMA)₃(H₂O)₅ (MODF-1): Calcd C, 53.13; H, 5.08; N, 6.97. Found C, 53.53; H, 5.61; N, 6.68. Discrepancy in formulation of guests in MODF-1 using single-crystal X-ray diffraction and elemental microanalysis is due to inherent problems associated with their facile loss at room temperature and their extensive disorder in the solid state.

(10) A green needle crystal of MODF-1 was analyzed: orthorhombic, space group P2₁2₁2₁ with *a* = 20.3300(9) Å, *b* = 23.1692(11) Å, *c* = 32.0081(15) Å, *V* = 15076.8(12) Å³, *Z* = 4, *d*_{calc} = 0.900 g/cm³, and μ(Mo Kα) = 0.685 mm⁻¹. All measurements were made on a SMART CCD area detector with graphite-monochromated Mo Kα radiation. *R*₁ = 0.0885 and *R*_w (all data) = 0.2723.

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‡ All crystal structures may be viewed and manipulated at <http://www.umich.edu/~yaghigrp/structures.html>.

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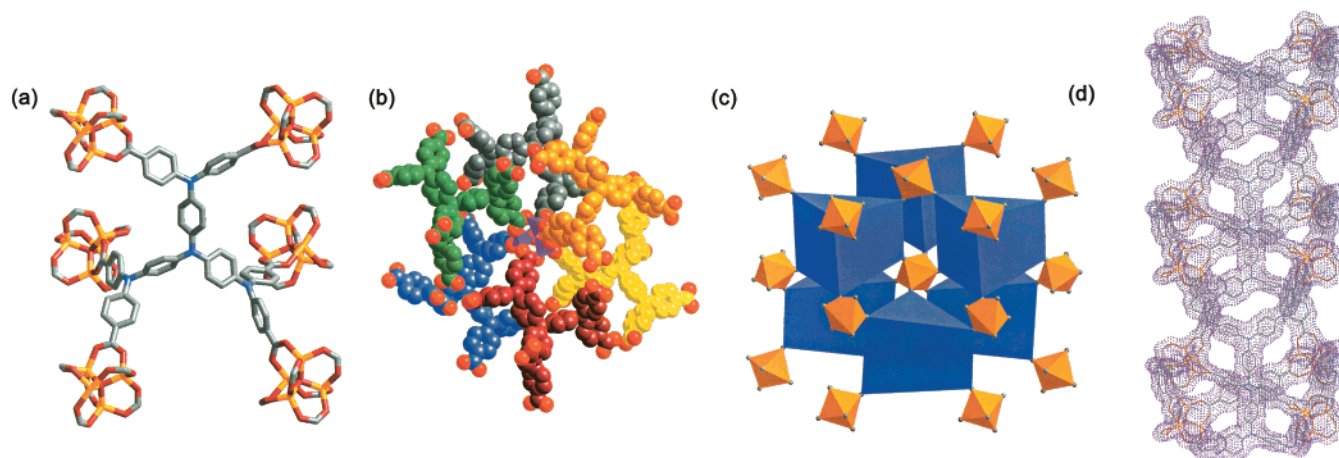


Figure 1. Crystal structure of MODF-1 showing the connectivity around (a) the TTA dendrimer and (b) the basic zinc acetate cluster building blocks (Zn, orange in (a) and magenta polyhedra in (b); C, gray in (a) but shown in space-filling style with six different colors in (b); O, red; N, blue, which respectively form (c) trigonal prismatic TBUs (blue) and octahedral SBUs (orange) that are reticulated into a NiAs-type structure having (d) a 3-D chiral channel system. (all hydrogen atoms, guests, and DMA ligands have been omitted for clarity).

The crystal structure of MODF-1 shows a 3-D porous framework that is created by linking the branched organic unit with Zn(II) ions at each of the six carboxylate termini (Figure 1). The asymmetric unit is composed of one TTA linker, one Zn_4O cluster, and two DMA ligands. Each carboxylate of TTA bridges two zinc ions that are each part of a basic zinc acetate-type cluster^{5a,11} containing four tetrahedral Zn centers surrounding a central oxide. Two terminal DMA ligands are bound to one of the zinc centers in the cluster (Figure 1a). In other words, each carboxylate lies on the edge of a Zn_4O group to produce an octahedral arrangement of carboxylates (Figure 1b).

Triarylamines crystallize with propeller structures, and this feature is present in the linkers of MODF-1. Within the TTA dendrimer, the central N lies in the same plane as the three outer N atoms. Each aryl ring of the triarylamine unit is canted by 15–45° to relieve repulsion between ortho-H atoms of the benzene units and create C–H... π interactions (3.827 (8)–3.841 (8) Å). The N atoms are nearly planar and lie only short distances from the triangular plane of the three *ipso* C atoms (0.097 (2)–0.250 (3) Å) bound to the nitrogen.

The dihedral angles between the benzene units create the linker's 3-D structure in which the set of carboxylate C atoms form a slightly distorted, large trigonal prism with edge dimensions ranging from 9.693 to 15.893 Å (Figure 1c). The trigonal prismatic units of MODF-1 contain nine branching phenylene units, which can be considered tertiary building units (TBUs).¹² The presence of trigonal prismatic and octahedral building units^{4b} rationalizes the NiAs topology¹³ found in MODF-1 (Figure 1c). The resulting framework contains a labyrinth of chiral channels that are between 8 and 17 Å in diameter and contain at least three DMA and 21 water molecules per formula unit (Figure 1d).

A division of the crystal volume into void volume (70%), organic matter (25%), and Zn_4O clusters (5%) shows that the bulk of the material is void volume and organic matter. To evaluate

the stability of MODF-1, we conducted, under inert atmosphere, thermal gravimetric analysis of crystalline MODF-1 (5.328 mg). We heated the sample from 20 to 700 °C at 10 °C/min. The sample lost weight immediately. A sharp decrease in weight was observed at 50 °C, and this decrease continued slowly up to 300 °C. The total mass loss was 28.3%, which corresponds to dissociation of two DMA ligands and the three DMA and five H₂O guests in each formula unit (Calcd: 28%). A further decrease in weight 53.3% occurred between 400 and 600 °C, corresponding to loss of the TTA unit (55%) and decomposition of the material.

To confirm the stability of this evacuated framework and evaluate its permanent porosity, we measured its gas sorption isotherm. MODF-1 (40 mg, ca. 0.01 mm size particles) was evacuated at 5×10^{-5} Torr and 25 °C for 20 h in a microbalance (CAHN 1000) using published methods.⁵ Sorption isotherms for gases or vapors of N₂, Ar, CH₂Cl₂, CCl₄, C₆H₆, and C₆H₁₂. All isotherm plots of (mg sorbed)/[g of MODF-1] vs P/P_0 (P_0 = saturation pressure of sorbate) showed type-I sorption behavior, indicating that evacuated MODF-1 has permanent porosity. Similar to those of zeolites and porous MOFs, the isotherms of MODF-1 are reversible and show no hysteresis upon desorption of sorbates from the pores. A pore volume of 0.26 cm³/g and an estimated surface area of 740 m²/g were calculated from the N₂ isotherm.

This report demonstrates the potential of using branched organic building blocks to link inorganic clusters and provide *crystalline* frameworks.

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Supporting Information Available: Preparation and characterization of H₆TTA, crystallographic data, bond lengths and bond angles, including FT-IR data and sorption isotherms for MODF-1 (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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