

Covalent 3- and 2-Dimensional Titanium–Quinone Networks

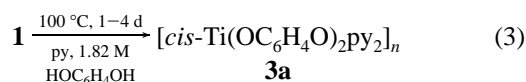
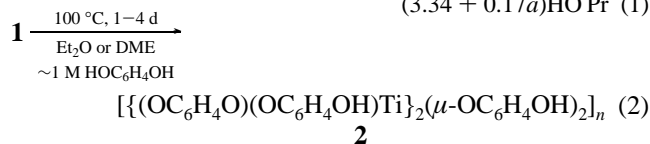
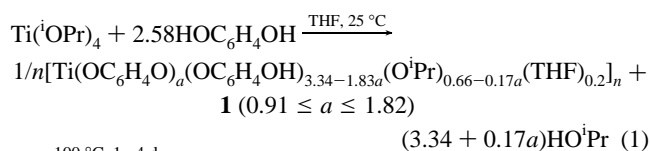
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Extended 3- and 2-dimensional networks derived from transition or main group metals combined with ligands possessing multiple binding sites comprise a forefront area of research in solid state chemistry.^{1–3} Networks have been constructed from 4,4'-bipyridine,^{4–7} pyrazines,^{6–10} pyrimidine,¹¹ cyanide,^{3,12–14} azide,¹⁵ and larger, more elaborate organic spacers.^{3,16–20} For example, tetra(*p*-cyanophenyl)methane combines with Cu⁺ to form a predicted diamondoid network,³ and 1,3,5-(N≡CC≡C)₃C₆H₃²⁰ spans Ag⁺ in extending a ThSi₂ structural motif to the metal–organic realm. The critical fusion of metal and organic spacer is usually accomplished through a framework of dative bonds; consequently, degradation pathways based on ligand dissociation or solvolysis may be present. Strong, covalent²¹ titanium/quinone linkages chosen to encourage intermetallic communication (i.e., Ti^{IV}-OC₆H₄O-Ti^{IV} ↔ Ti^{III}-O=CC₆H₄C=O-Ti^{III}) are the crucial connections for the dense networks reported herein.

Using a modified procedure of Burch,²² Ti(^{*i*}OPr)₄ was treated with 2.58 equiv of hydroquinone in THF to yield an amorphous (XRD), red-orange powder upon drying (eq 1). After the



powder was quenched with D₂O/DCl, ¹H NMR spectroscopic analysis of the DOC₆H₄OD/DO^{*i*}Pr/THF ratio revealed the empirical formula indicated (1). Addition of HOC₆H₄OH to **1** in various solvents (~1 M) enabled a conversion to burgundy, microcrystalline compounds upon thermolysis at 100 °C for 1–4

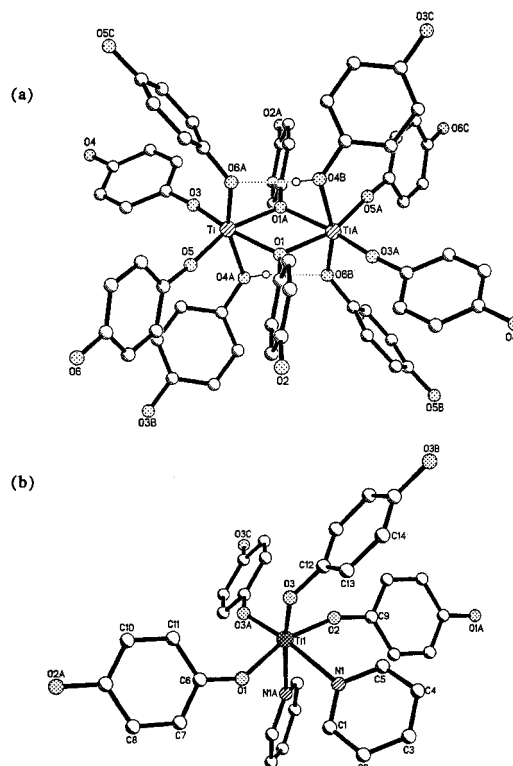


Figure 1. (a) Biocahedral ditanium building block of $[\{(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{OH})\text{Ti}\}_2(\mu\text{-OC}_6\text{H}_4\text{OH})_2]_n$ (**2**) with all bridges included (distances in Å, angles in deg): O1–Ti–O3 = 166.2(2); O1–Ti–O4A = 76.4(2); O1–Ti–O5 = 92.5(2); O1–Ti–O6 = 85.5(2); O1A–Ti–O3 = 93.1(2); O1A–Ti–O4A = 76.4(2); O1A–Ti–O5 = 161.1(2); O1A–Ti–O6A = 89.4(2); O3–Ti–O4A = 92.2(2); O3–Ti–O5 = 99.8(2); O3–Ti–O6A = 98.0(2); O4A–Ti–O5 = 89.3(2); O4A–Ti–O6A = 163.0(2); O5–Ti–O6 = 102.3(2). (b) Distorted octahedral building block of $[\text{cis-Ti}(\text{OC}_6\text{H}_4\text{O})_2\text{py}_2]_n$ (**3a**) with all bridges included: O1–Ti–O3 = 94.3(2); O1–Ti–N1 = 82.9(2); O2–Ti–O3 = 95.8(2); O2–Ti–N1 = 85.2(2); N1–Ti–O3 = 94.3; N1–Ti–O3A = 170.6(2).

d. Hydroquinone presumably deaggregates **1**, leading to sparingly soluble mono- or ditanium fragments that can be reconstituted into distinct microcrystalline networks.

Single-crystal X-ray diffraction studies of materials derived from Et₂O (**2**, eq 2) and pyridine (**3a**, eq 3) revealed dramatic solvent-dependent changes in the dimensionality and connectivity of the metal–organic network. The crystal size (20 × 20 × 60 μm) of $[\{(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{OH})\text{Ti}\}_2(\mu\text{-OC}_6\text{H}_4\text{OH})_2]_n$ (**2**) required data acquisition via a synchrotron source (CHESS).²³

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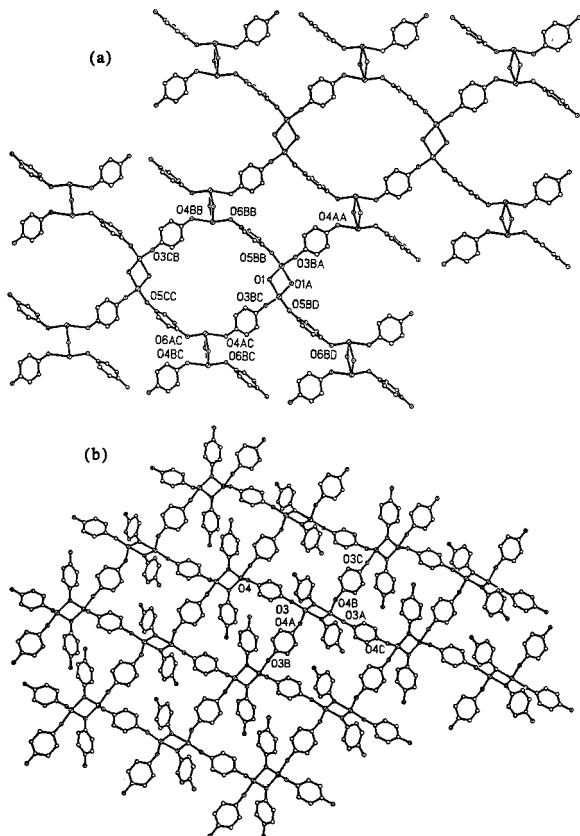


Figure 2. (a) One of the two nets showing the axial (O4, O6) to equatorial (O3, O5) connectivity of $[(\text{OC}_6\text{H}_4\text{O})(\text{OC}_6\text{H}_4\text{OH})\text{Ti}]_2(\mu\text{-OC}_6\text{H}_4\text{OH})_2)_n$ (**2**); the $\mu\text{-OC}_6\text{H}_4\text{OH}$ bridges have been removed for clarity. (b) The 4-hydroxyphenoxide (O3, O4) net of **2**; the 1,4-diphenoxide (O5, O6) net is similar.

Its 3-dimensional network is roughly derived from a body-centered arrangement of bioctahedral ditanium building blocks (Figure 1a, cf., $[(\text{PhO})_3(\text{PhOH})\text{Ti}]_2(\mu\text{-OPh})_2$,²⁴ $[(\text{PhO})\text{Cl}_2\text{Ti}]_2(\mu\text{-OPh})_2$)²⁵ connected via 1,4-diphenoxide (O5, O6) and 4-hydroxyphenoxide (O3, O4) ligands, while the 4-hydroxyphenoxide bridges of each dimer fill void space. In Figure 2a, axial 1,4-diphenoxide ($d(\text{Ti}-\text{O}6) = 1.923(3)$ Å, $\angle\text{Ti}-\text{O}6-\text{C}16 = 129.3(3)^\circ$) and 4-hydroxyphenoxide ($d(\text{Ti}-\text{O}4) = 2.207(3)$ Å, $\angle\text{Ti}-\text{O}4-\text{C}10 = 125.9(3)^\circ$) ligands that hydrogen bond²⁶ form one planar net by linking via the equatorial sites ($d(\text{Ti}-\text{O}5) = 1.794(4)$ Å, $\angle\text{Ti}-\text{O}5-\text{C}13 = 164.1(3)^\circ$; $d(\text{Ti}-\text{O}3) = 1.782(3)$ Å, $\angle\text{Ti}-\text{O}3-\text{C}7 = 173.0(3)^\circ$) of adjacent $\text{Ti}_2(\mu\text{-OC}_6\text{H}_4\text{OH})_2$ units. In another view (Figure 2b), the planar net derived solely from the 4-hydroxyphenoxide ($\text{O}3_{\text{eq}}$, $\text{O}4_{\text{ax}}$) is constructed, and the bridging 4-hydroxyphenoxides ($d(\text{Ti}-\text{O}1) = 2.047(3)$, $2.042(3)$ Å; $\text{Ti}-\text{O}1-\text{Ti}A = 106.5(2)^\circ$; $\text{O}1-\text{Ti}-\text{O}1A = 81.5(2)^\circ$) are shown as filling the void space in this dense network.

A relatively high concentration of $\text{HOC}_6\text{H}_4\text{OH}$ in pyridine (1.82 M) converted **1** to red crystals (<30 μm) of **3a** ($>98\%$, eq 3), while lower concentrations (0.55 M) afforded green/black **3b** in $>95\%$ yield. Synchrotron data acquisition and structure solution revealed a 2-dimensional, pleated sheet structure for $[\text{cis-Ti}(\text{OC}_6\text{H}_4\text{O})_2\text{py}]_n$ (**3a**).²⁷ A relatively linear strand of *trans*-1,4-diphenoxides ($\angle\text{O}1-\text{Ti}-\text{O}2 = 163.7(3)^\circ$, $\angle\text{Ti}-\text{O}1-$

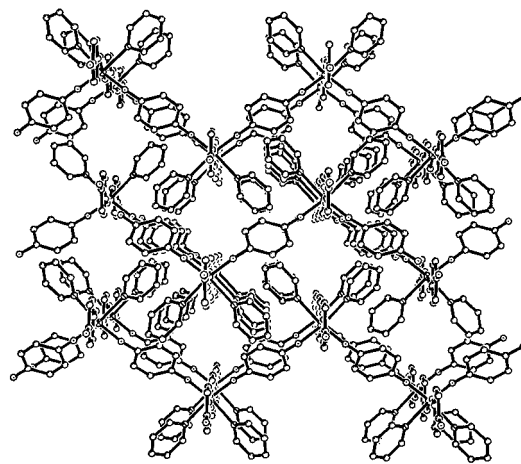


Figure 3. Stacking of the 2-D, pleated sheet of $[\text{cis-Ti}(\text{OC}_6\text{H}_4\text{O})_2\text{py}]_n$ (**3a**).

$\text{C}6 = 143.3(6)^\circ$, $\angle\text{Ti}-\text{O}2-\text{C}9 = 161.0(5)^\circ$, $d(\text{Ti}-\text{O}1) = 1.915(6)$ Å, $d(\text{Ti}-\text{O}2) = 1.875(6)$ Å) connect distorted octahedral titanium centers (Figure 1b) in one dimension, while a zigzag chain of *cis*-1,4-diphenoxides ($\angle\text{O}3-\text{Ti}-\text{O}3A = 103.3(3)^\circ$, $\angle\text{Ti}-\text{O}3-\text{C}12 = 137.4(4)^\circ$, $d(\text{Ti}-\text{O}3) = 1.883(4)$ Å) establishes the second (Figure 3). *cis*-Pyridines ($d(\text{Ti}-\text{N}) = 2.316(6)$ Å, $\text{N}1-\text{Ti}-\text{N}1A = 84.9(3)^\circ$) alternate with the arenes of the zigzag *cis*-1,4-diphenoxide chain in order to efficiently pack the sheets together, but their respective π -systems do not stack. The triclinic unit cell of **3b**²⁸ can accommodate the $[\text{Ti}(\text{OC}_6\text{H}_4\text{O})_2\text{py}_2\text{py}]_n$ formula unit ($\rho_{\text{calcd}} = 1.32$ g/cm³) suggested from quenching studies. Thermolysis of **3b** (1.82 M $\text{HOC}_6\text{H}_4\text{OH}$, pyridine) ultimately afforded **3a**, which did not revert to **3b** under a variety of conditions.

The diverse structures of $[(\text{OC}_6\text{H}_4\text{O})_2(\text{OC}_6\text{H}_4\text{OH})_2\text{Ti}_2(\mu\text{-OC}_6\text{H}_4\text{OH})_2)_n$ (**2**) and $[\text{cis-Ti}(\text{O}-\text{C}_6\text{H}_4\text{O})_2\text{py}]_n$ (**3a**) and the other, distinct derivatives derived from THF, CH_3CN , EtCN ,²⁹ and various hydroquinones portend a rich structural chemistry for these covalently linked, robust, metal-organic networks. Efforts are currently being directed toward imparting properties to these dense, hybrid^{30,31} solids: (1) alkali metal doping of **2** to afford ion conductivity or reduced titanium centers for conductivity; (2) intercalation chemistry of **3a,b**; and (3) synthesis of d¹ vanadium analogues and vanadium-doped networks for electronic properties.

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Supporting Information Available: X-ray structural data pertaining to $[(\text{OC}_6\text{H}_4\text{O})_2(\mu\text{-1,4-OC}_6\text{H}_4\text{-OH})_2\text{Ti}_2(\mu\text{-OC}_6\text{H}_4\text{OH})_2)_n$ (**2**) and $[\text{cis-Ti}(\text{OC}_6\text{H}_4\text{O})_2\text{Ti}(\text{py})_2]_n$ (**3a**) and a summary of crystallographic parameters, atomic coordinates, bond distances and angles, and anisotropic thermal parameters (12 pages). See any current masthead page for ordering and Internet access instructions.

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(23) For **2**: empirical formula, $\text{C}_{18}\text{H}_{14}\text{O}_6\text{Ti}$; fw, 374.19; $T = 110(2)$ K; $\lambda = 0.98000$ Å; monoclinic, $P2_1/n$; $a = 9.624(2)$ Å, $b = 11.283(2)$ Å, $c = 14.916(3)$ Å; $\beta = 90.47(3)^\circ$; $Z = 4$; $V = 1619.6(5)$ Å³; $\rho_{\text{calcd}} = 1.535$ g/cm³; abs. coeff., 0.561 mm⁻¹; 1451 reflections; GOF on F^2 , 1.061; $R_1 = 0.0751$, $wR^2 = 0.2280$; calcd and exptl powder XRD matched.

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(27) For **3a** ($30 \times 30 \times 30$ μm): empirical formula, $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_4\text{Ti}$; fw, 420.27; $T = 293(2)$ K; $\lambda = 0.9140$ Å; orthorhombic, $Pnma$; $a = 15.631(3)$ Å, $b = 14.017(3)$ Å, $c = 9.063(2)$ Å; $Z = 4$; $V = 1985.7(7)$ Å³; $\rho_{\text{calcd}} = 1.406$ g/cm³; abs. coeff., 0.462 mm⁻¹; 1318 reflections; GOF on F^2 , 1.224; $R_1 = 0.0858$, $wR^2 = 0.2338$; calcd and exptl powder XRD matched.

(28) For **3b** ($2\text{--}4$ μm, powder XRD): $a = 8.717(2)$ Å, $b = 8.803(2)$ Å, $c = 9.016(2)$ Å, $\alpha = 82.83(2)^\circ$, $\beta = 75.36(2)^\circ$, $\gamma = 71.09(2)^\circ$; $V = 632.6$ Å³.

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