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Hydrogen bonds between polyphenol ($(p\text{-HOC}_6\text{H}_4\text{O})_6\text{W}$) and bipyridines: ($4,4'\text{-bipy}\cdot\text{HOC}_6\text{H}_4\text{O})_6\text{W}$ and 3-D networks $[\{4,4'\text{-(NC}_5\text{H}_4)_2(\text{CH}_2\text{CH}_2)\}_n\{(\text{HOC}_6\text{H}_4\text{O})_6\text{W}\}]_\infty$ ($n = 2, 3$)

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Polyphenol ($(p\text{-HOC}_6\text{H}_4\text{O})_6\text{W}$) is stable with respect to condensation, and formed ($4,4'\text{-bipy}\cdot\text{HOC}_6\text{H}_4\text{O})_6\text{W}$ and the 3-D networks $[\{4,4'\text{-(NC}_5\text{H}_4)_2(\text{CH}_2\text{CH}_2)\}_n\{(\text{HOC}_6\text{H}_4\text{O})_6\text{W}\}]_\infty$ ($n = 2, 3$), when treated with 4,4′-bipy and 1,2-di-4-pyridylethane, respectively.

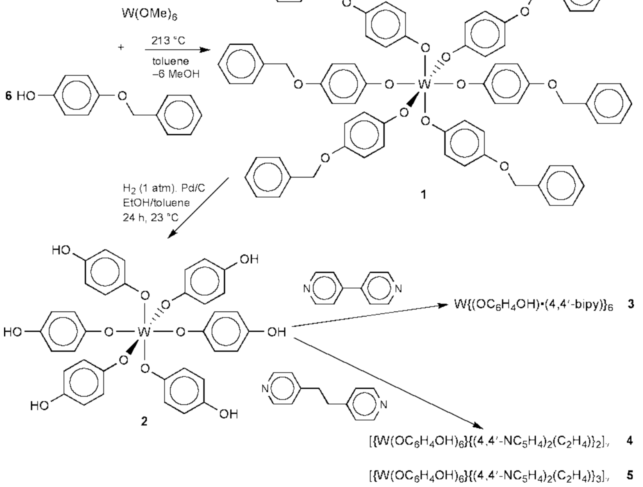
The construction of coordination networks[1] and dendrimeric materials[2,3] often utilizes a polyfunctionalized molecular core from which branches may emanate. While such organic cores exhibit various functionalities, inorganic equivalents are less structurally diverse, and most metals can be considered as Lewis acidic nodes amidst an organic framework. Creating functionality pendant to a metal can be a difficult problem,[4] especially for early transition metals, which are intolerant to many groups. For example, modeling studies indicated that $(4\text{-HO-}2,6\text{-C}_6\text{R}_2\text{H}_2\text{O})_4\text{M}$ (M = Ti, Zr) would be effectively blocked from self-condensations *via* appropriately sized substituents R, yet trace $4\text{-HO-}2,6\text{-C}_6\text{R}_2\text{H}_2\text{OH}$ and rapid alkoxide exchange chemistry hampered all efforts at isolating such species, and oligomeric materials were obtained.

In contrast, $(\text{PhO})_6\text{W}$[5] is known to be stable in basic media, and is only susceptible to acid catalyzed phenoxide exchange at elevated temperatures.[6] The innate stability of hexaphenoxidetungsten complexes suggested a route to a polyhydroxylated inorganic core, namely $(p\text{-HOC}_6\text{H}_4\text{O})_6\text{W}$.

As Scheme 1 illustrates, treatment of W(OMe)_6, prepared from $\text{W(OMe)}_4\text{Cl}_2$, MeOH and NEt_3,[7] with $p\text{-HOC}_6\text{H}_4\text{OCH}_2\text{Ph}$ in toluene for 24 h at 213 °C in a bomb reactor yielded the polybenzyl ether, $(p\text{-PhCH}_2\text{OC}_6\text{H}_4\text{O})_6\text{W}$ **1** (91%).† Deprotection was effected *via* hydrogenation (H_2 (1 atm), Pd/C) in ethanol–toluene, and dark red $(p\text{-HOC}_6\text{H}_4\text{O})_6\text{W}\cdot 2\text{THF}\cdot\text{C}_6\text{H}_6$ (**2**$\cdot 2\text{THF}\cdot\text{C}_6\text{H}_6$) was crystallized in 60% yield from THF–benzene.† An intricate, three-dimensional hydrogen-bonding network[8] is observed for **2**$\cdot 2\text{THF}\cdot\text{C}_6\text{H}_6$.‡ Fig. 1. reveals rings of $(p\text{-OH})_4$ that comprise one connectivity, another loop that alternately involves two *p*-OH and two phenoxide oxygens, and a single *p*-OH···THF hydrogen bond. The WO···HO hydrogen bond renders the W–O2 bond long (1.934(4) Å) in contrast to the 1.889(14) Å average distance of the normal tungsten aryloxide bonds.[9] The W–O–C angles range from 136.8(4) to 148.0(4)° to accommodate the network, and little distortion from octahedral coordination is observed in the WO_6 core ($\angle\text{OWO}_{cis} = 90.0(21)°_{\text{av}}$; $\angle\text{OWO}_{trans} = 176.7(24)°_{\text{av}}$).

Attempts to generate a hydrogen-bonded network[8] from $(p\text{-HOC}_6\text{H}_4\text{O})_6\text{W}$ **2** and 4,4′-bipyridine failed when efforts to control stoichiometry continually led to the hexa-4,4′-bipyridine derivative $(4,4'\text{-bipy}\cdot\text{HOC}_6\text{H}_4\text{O})_6\text{W}$ **3** (Scheme 1, Fig. 2).‡ Hexabasic **3** has a regular core ($\angle\text{OWO}_{cis} = 90.0(7)°_{\text{av}}$; $\angle\text{OWO}_{trans} = 178.8(2)°_{\text{av}}$; $d(\text{W–O}) = 1.901(10)$ Å$_{\text{av}}$; $\angle\text{WOC} = 137.8(16)°_{\text{av}}$), and packs in hexagonal columns due to face-to-face π-stacking interactions of the bipyridines.[10]

Concern that 4,4′-bipy was rendered an ineffective linker due to the weaker basicity of the second nitrogen upon formation of the initial hydrogen-bond, or its conformational rigidity, prompted a change to 1,2-di-4-pyridylethane. When combined with $(p\text{-HOC}_6\text{H}_4\text{O})_6\text{W}\cdot 2\text{THF}\cdot\text{C}_6\text{H}_6$ **2**, two materials of stoichiometry $[\{4,4'\text{-(NC}_5\text{H}_4)_2(\text{CH}_2\text{CH}_2)\}_2\{(\text{HOC}_6\text{H}_4\text{O})_6\text{W}\}]_\infty$ **4** and $[\{4,4'\text{-(NC}_5\text{H}_4)_2(\text{CH}_2\text{CH}_2)\}_3\{(\text{HOC}_6\text{H}_4\text{O})_6\text{W}\}\cdot\text{THF}]_\infty$ (**5**·THF) were isolated in *ca.* 1:3 ratio (Scheme 1). Fig. 3(a) reveals the OH···N, N···HO bonds of **4** as a zigzag chain-link motif, while Fig. 3(b) shows how additional phenols interact with the OH groups of these units to form a box.‡ Similar H-bonds connect the boxes and a redundant network interpenetrates to form an overall doubly interpenetrating 3-D network.[1] Again the tungsten core is regular ($\angle\text{OWO}_{cis}$ =



Scheme 1

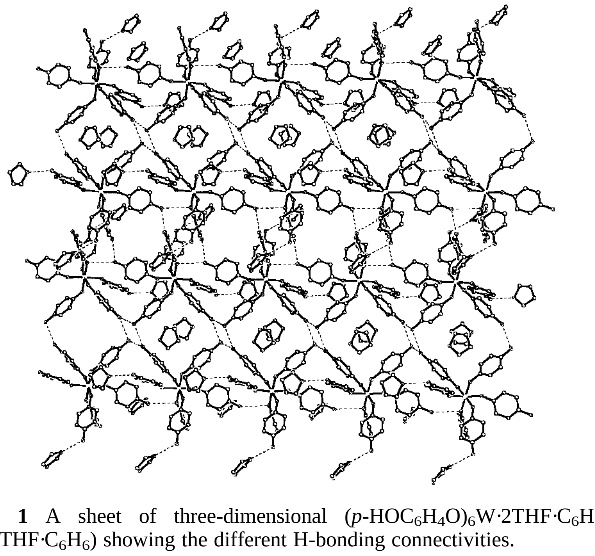


Fig. 1 A sheet of three-dimensional $(p\text{-HOC}_6\text{H}_4\text{O})_6\text{W}\cdot 2\text{THF}\cdot\text{C}_6\text{H}_6$ (**2**$\cdot 2\text{THF}\cdot\text{C}_6\text{H}_6$) showing the different H-bonding connectivities.

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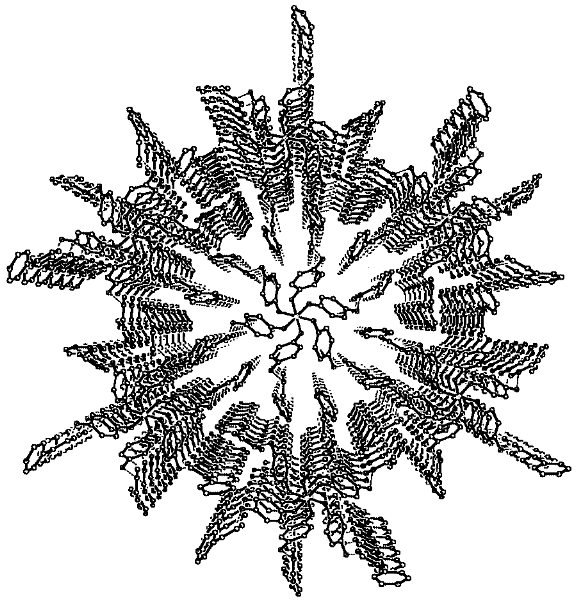

Fig. 2 The hexagonal columns of (4,4′-bipy·$HOC_6H_4O)_6W$ **3**.

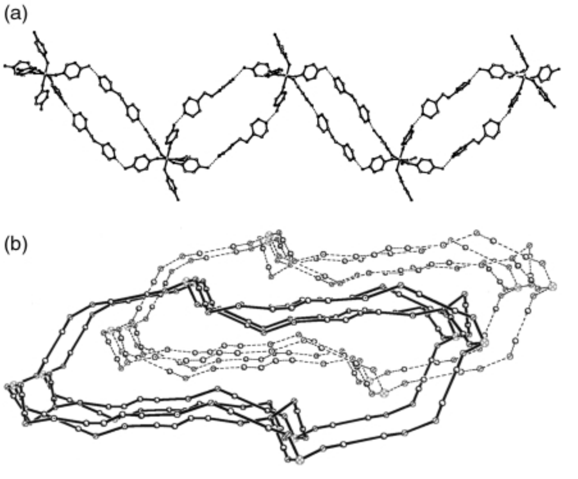

Fig. 3 (a) The zigzag OH···N, N···HO connectivity of $[\{4,4'\text{-}(NC_5H_4)_2(CH_2CH_2)\}_2\{(HOC_6H_4O)_6W\}]_\infty$ **4**. (b) Additional phenolic H-bonds generate the doubly interpenetrating three-dimensional boxes of **4** (W = ⊗, O = ⊘, N = ⊙, *p*-C and ethane carbons (○)).

90.0(18)°$_{av}$; ∠OWO_{trans} = 178.4(8)°$_{av}$; *d*(W–O) = 1.88(2) Å$_{av}$), but substantial variation in ∠WOC (143.6(54)°$_{av}$) is observed to reflect the constraints of the network.

Fig. 4(a) illustrates the connectivity of $[\{4,4'\text{-}(NC_5H_4)_2(CH_2CH_2)\}_3\{(HOC_6H_4O)_6W\}\cdot THF]_\infty$ (**5**·THF), whose tungsten centers are linked *via* OH···N, N···HO bonds to form an irregular box. The familiar octahedral core of the $(HOC_6H_4O)_6W$ group is evident (∠OWO_{cis} = 90.0(25)°$_{av}$; ∠OWO_{trans} = 177.6(17)°$_{av}$; *d*(W–O) = 1.86(5) Å$_{av}$), yet the W–O–C angles vary greatly (135.7(18)° to 169.4(19)°) to accommodate geometric features of the three-dimensional network. The box described above is voluminous, hence the structure triply interpenetrates[1] [Fig. 4(b)].

In summary, hexaphenol (*p*-$HOC_6H_4O)_6W$ **2** does not self-condense into μ-OC_6H_4O oligomers and can be utilized to form hydrogen-bonded complexes and networks.

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Notes and references

† *Selected analytical data*: **1** (acetone-d$_6$), δ_H 5.04 (2 H, s, CH_2), 6.87 (4 H, br s, OCHCHO), 7.4 (5 H, m, C_6H_5); δ_C 70.88 (CH_2), 115.77 (*m*-C_a), 121.96 (*o*-C_a), 128.48, 129.32 (*o*-C_b, *m*-C_b), 128.66 (*p*-C_b), 138.45 (*ipso*-C_b), 155.87, 157.13 (*ipso*-C_a, *p*-C_a). **2** (acetone-d$_6$), δ_H 6.72 (4 H, m, CH), 8.14 (1 H, s, OH); δ_C 115.82, 115.91 (*m*-C), 121.99 (*o*-C), 154.09, 154.19 (*p*-C), 156.39 (*ipso*-C), doubled resonances caused by OC_6H_4OD.

‡ *Crystal data*: **2**·2THF·C_6H_6: $C_{50}H_{52}O_{14}W$, *M* = 1060.77, triclinic, space group $P\bar{1}$, *a* = 10.3360(10), *b* = 11.8990(10), *c* = 21.761(3) Å, α = 97.120(10), β = 102.200(10), γ = 108.510(10)°, *U* = 2427.3(5) Å^3, *T* = 293(2) K, *Z* = 2, μ(Mo-Kα) = 2.444 mm^{-1}, 6303 (R_{int} = 0.0272) independent reflections, $R_1(2\sigma)$ = 0.0326. **3**: $C_{96}H_{78}N_{12}O_{12}W_5$, *M* = 1775.56, hexagonal, space group *R*3, *a* = 27.1402(1), *c* = 9.7013(1) Å, *U* = 6188.52(7) Å^3, *T* = 173(2) K, *Z* = 6, μ(Mo-Kα) = 1.473 mm^{-1}, 4778 (R_{int} = 0.0420) independent reflections, $R_1(2\sigma)$ = 0.0325. **4**: $C_{60}H_{54}N_4O_{12}W$, *M* = 1206.92, triclinic, space group $P\bar{1}$, *a* = 9.5723(3), *b* = 11.2623(4), *c* = 26.9897(9) Å, α = 86.9380(10), β = 83.5980(10), γ = 88.5040(10)°, *U* = 2886.79(17) Å^3, *T* = 296(2) K, *Z* = 2, μ(Mo-Kα) = 2.064 mm^{-1}, 9721 (R_{int} = 0.0502) independent reflections, $R_1(2\sigma)$ = 0.0740. **5**·THF: $C_{76}H_{74}N_6O_{13}W$, monoclinic, space group $P2_1/c$, *a* = 25.132(3), *b* = 11.6991(18), *c* = 25.988(4), β = 104.724(3)°, *U* = 7389.9(19) Å^3, *T* = 295(2) K, *Z* = 4, 3445 (R_{int} = 0.0731) independent reflections, $R_1(2\sigma)$ = 0.1002.

CCDC reference numbers 156504–156507. See http://www.rsc.org/suppdata/cc/b1/b100561h/ for crystallographic data in CIF or other electronic format.

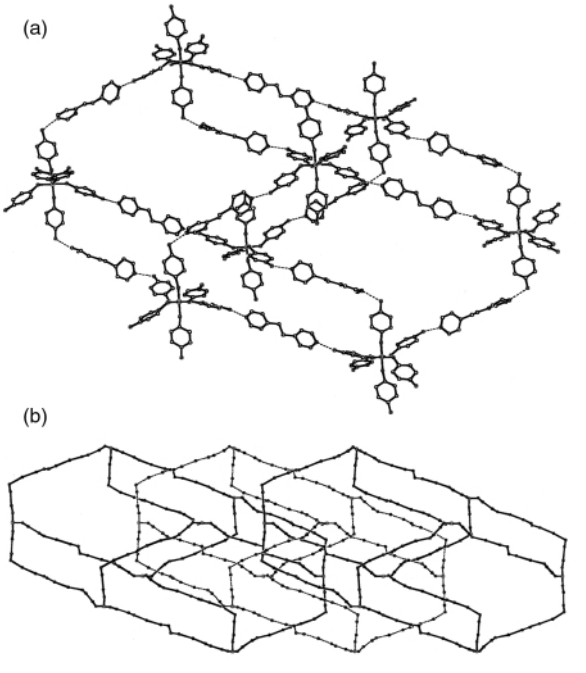

Fig. 4 (a) The OH···N, N···HO connectivity generating the irregular three-dimensional box of $[\{4,4'\text{-}(NC_5H_4)_2(CH_2CH_2)\}_3\{(HOC_6H_4O)_6W\}\cdot THF]_\infty$ **5**. (b) Triple interpenetration of the boxes W = ⊗, O = ⊘, N = ⊙, *p*-C and ethane carbons (○)).

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