Metal–Organic Nanotubes

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Isorecticular Synthesis of Dissectible Molecular Bamboo Tubes of Hexarhenium(I) Benzene-1,2,3,4,5,6-hexaolate Complexes

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Abstract: *A family of bamboo-like metal–organic nanotubes consisting of in situ synthesized macromolecular blocks (MB) is reported. The MBs are composed of six fac-$(CO)_3$Re cores, one benzene-1,2,3,4,5,6-hexaolate plate, and six pyridine-derivative pillar ligands, which have a doubly tri-legged geometry and can be mutually assembled, piece by piece. This entire system is characterized as a simple but precise supramolecular complexation of these macromolecular blocks and further introduces an archetypal approach to systematically constructing a tunable form of dissectible molecular bamboo tubes.*

Macromolecular architectures with spatially localized scaffolds have become a topic of intense interest, not only owing to their potential applications, ranging from sensors, separations, and catalysts,[1,2] but also because various molecular shapes can be easily designed, especially mimicking macro-objects, such as boxes, motors, boats, cars, and vessels.[3] Guided by biological principles, if any suitable molecular interlinking brick was synthesized, further conceivable assemblies would be expected to be generated. This approach is similar to the formation of many bio-structures only from a few simple molecules, such as amino acids, sugars, and related materials.[4] Since the pioneering work by Pedersen, Cram and Lehn on supramolecular chemistry,[5] the supramolecular complexation of significantly well-defined large molecular aggregates have been developed.[6] Molecular nanotubes with distinct pore channels represent a unique class of assemblies, which could behave as molecular capillaries, sieves, and biological models.[7,8] It is critical to know how those macromolecular aggregates of designable building units are formed based on characterizing lock-and-key strategies. Surprisingly, less effort has been directed to the systematic formation of metal–organic nanotubes (MONTs),[9] in particular, the synthesis of controllable MONTs that are dissectible is currently only a dream.[10]

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As part of our ongoing efforts in the design and synthesis of functional crystalline materials,[11] we report herein on the preparation of a family of metal–organic tubular assemblies, $\{(C_8H_{10})\subset[\mathbf{MB\text{-}1}]\}_n$ (**1**, Figure 1), [MB-1] (**1′**), $\{(C_8H_{10})\subset[\mathbf{MB\text{-}2}]\}_n$ (**2**), $[\mathbf{MB\text{-}2}]_n$ (**2′**), $[\mathbf{MB\text{-}3}]_n$ (**3**), all of which consist of in situ synthesized macromolecular blocks (MBs), having a general formula of $[\{Re(CO)_3\}_6(C_6O_6)(Py\text{-}R_n)_6]$. The MBs, all comprise six *fac*-$(CO)_3$Re(I) cores, one benzene-1,2,3,4,5,6-hexaolate plate (bho^{6-}, $C_6O_6^{6-}$), and six pyridine-derivatives (Py-R_n; $R_1 = CH_3CO$; $R_2 = C_6H_5$; $R_3 = H$), have a doubly tri-legged structure and can be mutually assembled, piece by piece, to form target molecular bamboo tubes (MBTs). This entire system is characterized as a simple but precise molecule-to-molecule complexation of these MBs and introduces an archetypal approach to the preparation of a new type of molecular aggregate. To our knowledge, such unique nanotubes, made up of a series of designable and isorecticular benzenehexaolate-based macromolecular blocks, is currently unprecedented.[11b,c,12]

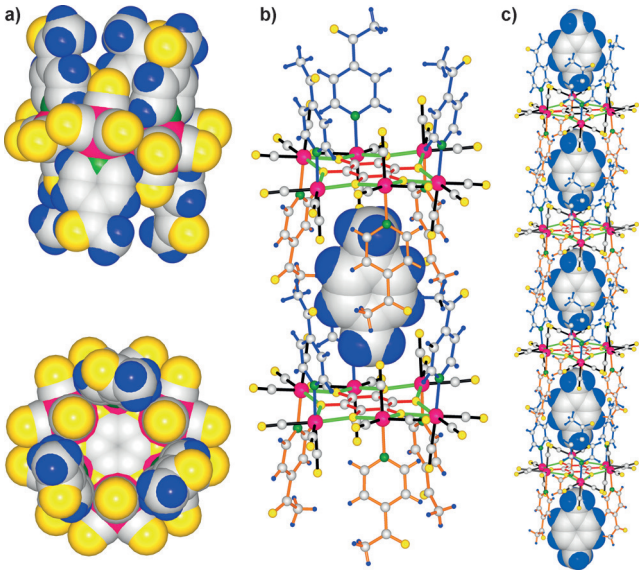
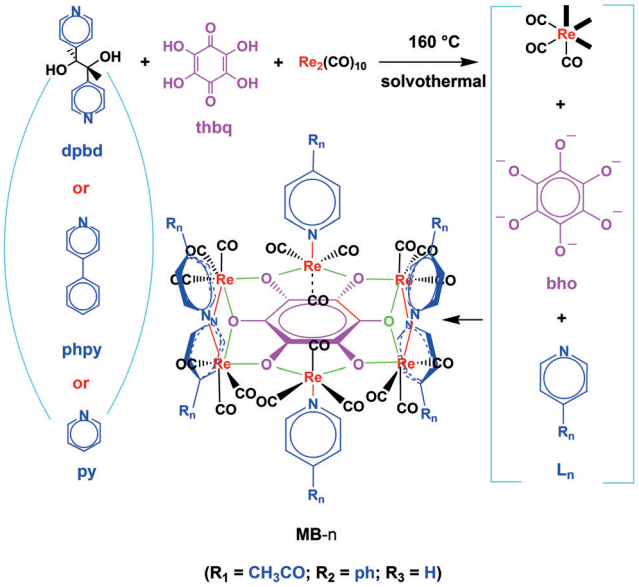


Figure 1. Structures of compound **1**: a) space-filling representations of side (upper structure) and top (lower structure) views of MB-1, b) molecule-to-molecule complexation of two interlocked MB-1 units, and encapsulated *p*-xylene guest c) ball-and-stick and space-filling mixing representation of MBT **1**. C gray, H blue, N green, O yellow, Re red.[18]

Compounds **1**–**3** and **1′**–**2′** were synthesized (see Experimental Section) by treating $Re_2(CO)_{10}$, 2,3,5,6-tetrahydroxybenzoquinone (thbq), and the pyridine-derived ligand in *p*-xylene (for **1**–**3**) or *m*-xylene (for **1′**–**2′**) through a one-step



Scheme 1. Synthesis of MBs-**1**–**3** (containing R_1–R_3, respectively) by one-step self-organization processes.

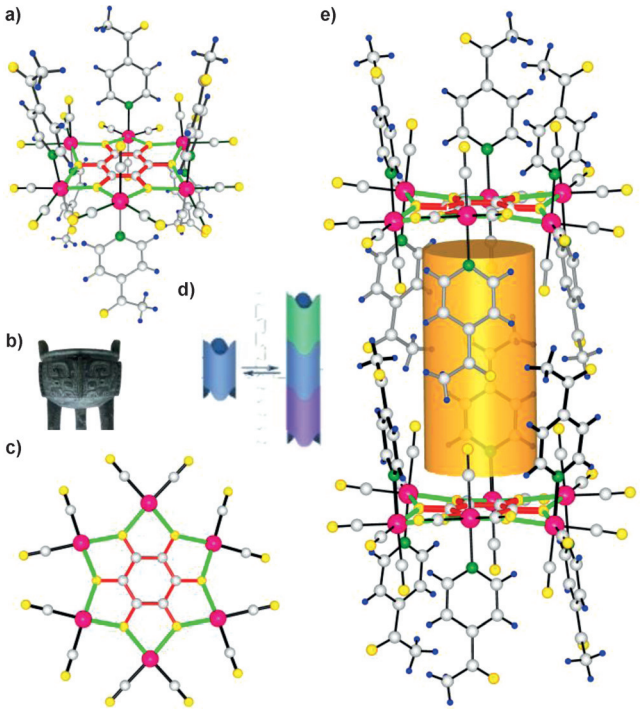


Figure 2. a) MB-1 unit with a doubly tri-legged structure. b) A Ding. c) Local coordination of the hexarhenium(I) benzene-1,2,3,4,5,6-hexaolate motif. d) An interlocking model. e) A capsule-like assembly of two MB-1 units containing a cylindrical void (highlighted in yellow).[18]

self-assembly process under solvothermal conditions, respectively (Scheme 1). These MBs all consist of thirteen components, including one benzenehexaolate (bho^{6-}) moiety, six *fac*-$Re(CO)_3$ cores, and six ancillary pillar ligands. The most intriguing feature of compounds **1** and **1′** is that all of the precursors were changed during the reaction—the bho^{6-} moiety was formed by the reduction of the thbq molecule; the acpy ligand was generated in situ from 2,3-di(pyridin-4-yl)butane-2,3-diol (dpbd), through an oxidative C–C bond cleavage. The preparation of MBs-2,3 was similar to MB-1. The combination of these two ligands (bho^{6-} and acpy) is chemically and structurally compatible. In particular, the bho^{6-} ligand was fortunately captured by six $(CO)_3Re^{I}$ moieties and six N-donor ligands. Interestingly, such a benzenehexaolate ($C_6O_6^{6-}$) ligand, to our knowledge, has never been reported in any organic compounds or transition-metal complexes and is observed here for the first time.[13] Unlike some similar chelating and bridging organic linkers, the bho^{6-} and pyridine-derived (Py-R_n) ligands favor the formation of a molecular bamboo-like structure, rather than a gondola, rectangle, or metalloprism.[14]

A single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the trigonal space group $R\bar{3}$. The asymmetric unit consists of one *fac*-$Re(CO)_3$ core, one-sixth of the bho^{6-} ligand, and one acpy ligand, and one-sixth of the *p*-xylene molecule. Each Re^{I} center is bound to three CO ligands, two oxygen atoms from the bho^{6-} ligand and one nitrogen atom from the acpy ligand in a distorted octahedral manner (Figure 2a). The bho^{6-} ligand was coordinated to six *fac*-$Re(CO)_3$ cores in a μ_6-$\kappa^2,\kappa^2,\kappa^2,\kappa^2,\kappa^2,\kappa^2$-mode (Figure 2c). The diagonal distance between the Re···Re atoms in this 12-membered Re_6O_6 ring is 8.12(3) Å. There are six 4-acetylpyridine (acpy) units coordinated to the six Re^{I} centers which are nearly perpendicular to the $C_6O_6^{6-}$ plate, each of the three acpy ligands resids on each side of the Re_6O_6 ring in a staggered configuration. Thus, MB-1 possesses a doubly tri-legged structure, in which there are three legs oriented upward and downward, respectively (Figure 2a). It resembles "a Ding", an ancient noble Chinese vessel (Figure 2b).

As shown in Figure 2d, these MB-1 units are stackable and can be mutually assembled in a staggered conformation using their three legs to an exact degree of precision. It is apparent that a cylindrical and capsule-like cavity with a volume of 704 $Å^3$ is formed (Figure 2e) and one *p*-xylene molecule, functioning as a glue, was precisely lodged in the capsule (Figure 1b). The acetyl groups of the acpy pillar ligands were all attached to the relevant oxygen atoms of the carbonyl groups. Thus, these interlocking MBs were able to regularly align as a linear supramolecular aggregate, analogous to a molecular bamboo tube (MBT)-the culm was the acpy ligands; the node was the $[\{Re(CO)_3\}_6(bho)]$ moiety (Figure 1c). The exterior wall diameter of the MBT is up to 15.4 Å, depending on the specific complex. Despite the height of an individual MB-1 unit, which is up to 17.4 Å, the separation of any two Re_6O_6 rings is merely 13.6 Å in the MBT. To our surprise, there were no significantly strong hydrogen bonding, π···π stacking, C–H···π interactions in the assembly.[15] Such a molecule-to-molecule complexation of the MB-1 units is unique and apparent only because of their doubly tri-legged structure and the existence of abundant van der Waals intramolecular interactions.

Compound **1′** (prepared in *m*-xylene) also crystallizes in the trigonal space group $R\bar{3}$, but the unit cell parameters were completely different from those of compound **1** (prepared in *p*-xylene. Its asymmetric unit consists of only one-sixth of the

MB-1 unit, as expected. Its molecule-to-molecule complexation is completely different from those of **1**. Because there were no trapped guest molecules, the acpy ligands truly bend inward, forcing the MB-1 unit in **1′** to assume a closed form (Figure 3a). The related angle of the acpy ligand and the

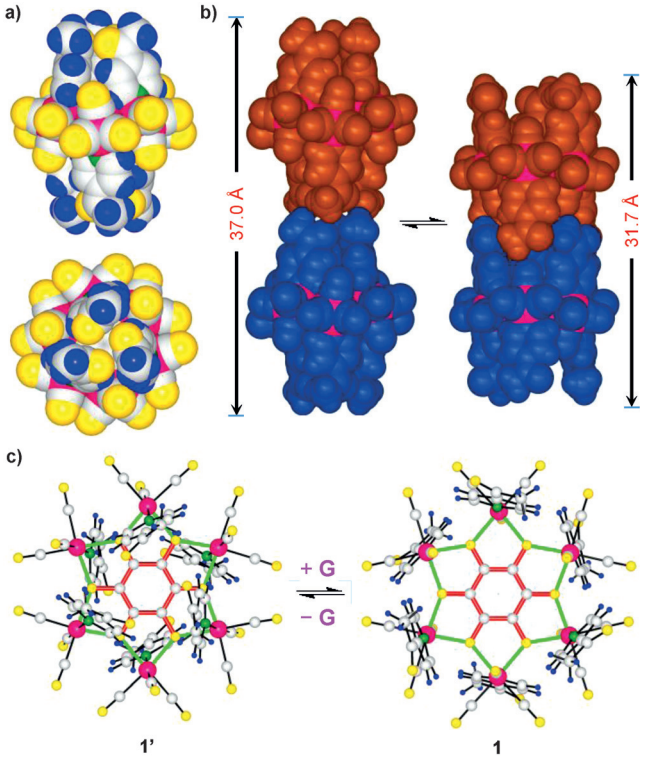


Figure 3. a) Space-filling representations of side (upper structure) and top (lower structure) views of MB-1 in **1′**. b) Mutually interlocking patterns of MB-1 in **1′** (left) and **1** (right). c) Two forms of MB-1: a closed form in **1′** and an open-form in **1**, *G* = *p*-xylene.[18]

[{Re(CO)$_3$}$_6$(bho)] in **1′** is merely 75.7(3)°, which is smaller than that of **1**, 89.8(1)°. The MB-1 units in **1′** are all non-interlocking and the height of each two staggered MB-1 units is up to 37.0(1) Å (Figure 3b), which is longer than that of **1** with 31.7(1) Å. That is to say because the biting angles between the acpy ligands and the [{Re(CO)$_3$}$_6$(bho)] nodes are flexible, the MB-1 molecule exhibits a dynamic behavior in the open and closed forms (Figure 3c).[16] Further analysis of this structure indicated that these MB-1 units in **1′** are merely attached to each other in a head-to-tail manner and not mutually interlocking at all. The structural differences between **1** and **1′** was also shown when compound **1** was heated under reflux in 1,3,5-mesitylene, these interlocking MB-1 units were completely disassembled, and then can further self-assemble and crystalize as compound **1′**.

Compounds **2**, **2′**, and **3** all crystallize in the trigonal space group $R\bar{3}$ and consist of their related MB units. In particular, the MB-2 units were all interlocked in both compounds **2** and **2′** in MBT manner, as mentioned above, irrespective of whether the *p*-xylene guest molecules were trapped or not (Figures 4b,c). The separations between two bamboo nodes

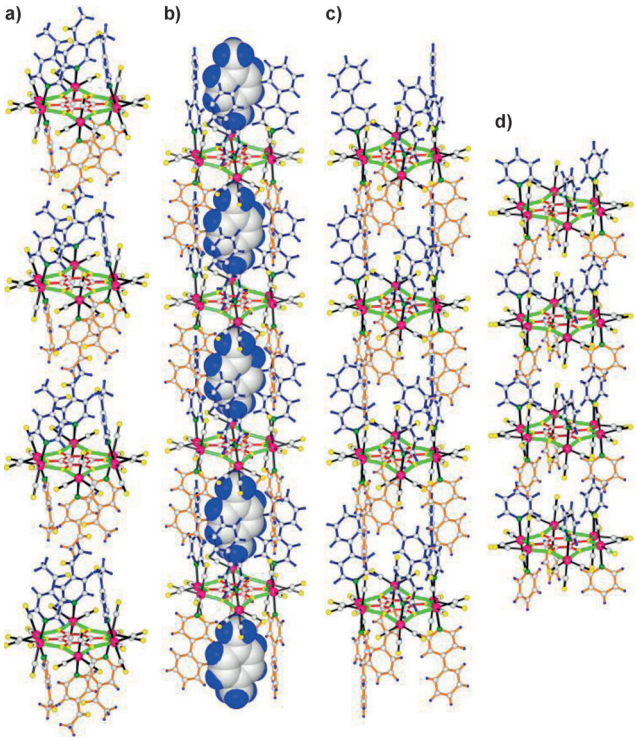


Figure 4. Molecule-to-molecule supramolecular complexations giving the bamboo-type assemblies: a) MB-1 in **1′**, b) MB-2 in **2**, c) MB-2 in **2′**, d) MB-3 in **3**.[18]

in **2** and **2′** are nearly the same, 14.96 Å and 15.09 Å, respectively. These molecule-to-molecule complexations were different from the MB-1 units in **1** and **1′**. The supramolecular complexation of MB-2 in **2** and **2′** is further advanced, mainly because the phpy ligand is longer than the acpy ligand and provides more intramolecular van der Waals interactions. Their dynamic behaviors were also evidenced, when compound **2′** was heated under reflux in *p*-xylene, the *p*-xylene molecules were trapped to form compound **2**. Even if the pyridine ligand is the shortest, the MB-3 units are still able to be assembled from each other (Figure 4d). This is the most primitive pattern among these MBT-type structures system.

The heights of the individual units of MB-2 in **2**, **2′**, and MB-3 are 21.1 Å, 21.2 Å, and 14.1 Å, respectively. The separation distances between each bamboo joint of compounds **1**, **1′**, **2**, **2′**, and **3** are 13.59, 17.63, 14.96, 15.09, and 11.29 Å, respectively, which all equal to one *c* translation. The longer the pillar ligands are, the longer the stems of the MBTs become; the larger the nodes, the larger the diameters are achieved. MBs-1–3 represent an original type of macromolecular building block, and further advanced supramolecular aggregates would be expected to be patterned and synthesized. The challenge now would be how to prepare these patterned MBs with larger and larger sizes, controllable interlocking abilities, and designable functionalities.

The building blocks of these nanotubes exhibit dynamic properties that allow the disassembly and reconstruction of the nanotubes from the discrete, non-interlocked [{Re(CO)$_3$}$_6$(C$_6$O$_6$)(Py-R$_n$)$_6$] unit. More importantly, the *p*-xylene molecule is specific and plays a key role in controlling these

switching processes. In addition, other solvents, such as benzene, toluene, or *o*-xylene, failed in similar reactions. The fact that the nanocapsules of **1** and **2** selectively recognize *p*-xylene is remarkable. As a consequence, the exchange and removal of guest *p*-xylene molecules during the conversion between **1** and **1′**, as well as **2** and **2′** could be observed based on structural changes. These molecular trains may haul specialized molecules in purpose-designed cars. In other words, the MBTs exhibit a selective host–guest recognition and have the potential to be used as molecular vehicles or in drug delivery.[17] The remaining striking feature lies in these hexarhenium(I) benzene-1,2,3,4,5,6-hexaolate complexes, not only owing to the rare form of their molecular structures, but also because they may have many unexplored and unexpected properties, such as in the fields of electrochemistry, spectroelectrochemistry.

In summary, we successfully synthesized a family of dissectible bamboo-like metal–organic nanotubes constructed of in situ generated benzenehexaolate (bho^{6-}; $C_6O_6^{6-}$)-based scaffolds, which have a doubly tri-legged geometry and were assembled piece by piece. These molecular bamboo nanotubes are dissectible and can be completely recoupled again. It is of fundamental interest that this synthetic strategy is a general one and the benzenehexaolate ligand is unprecedented and unknown for transition metal complexes. The entire system is characterized by a simple but precise molecule-to-molecule complexation. This finding offers an archetypal approach to the systematic construction of dissectible "train-like" molecular tubes. We believe that these designable materials will have great potential in the future. Further research is currently underway.

Experimental Section

Compound **1**, $\{(C_8H_{10})\subset[MB\text{-}1]\}_n$: A mixture of $Re_2(CO)_{10}$ (65.3 mg, 0.100 mmol), 2,3,5,6-tetrahydroxybenzoquinone (20.8 mg, 0.121 mmol), and 2, 3-di(pyridin-4-yl)butane-2,3-diol (dpbd, 24.4 mg, 0.100 mmol; obtained from Sigma–Aldrich as a 97% *meso* and 3% *rac* isomeric mixture) in *p*-xylene (6 mL) was sealed in a 23-mL Teflon-lined stainless steel Parr acid digestion bomb and heated at 160 °C for 72 h, and then slowly cooled to room temperature for 72 h. Dark-red block crystals were collected by filtration and washed with hexane, and only slightly dried in air. Yield 13.2% (34.5 mg, based on $Re_2(CO)_{10}$). Elemental analysis (%) for $C_{74}H_{52}N_6O_{30}Re_6$: calcd C 33.89, H 2.00, N 3.20; found C 33.69, H 2.06, N 3.24. Compound **1′**, [MB-1], was synthesized under the reaction conditions similar to that of **1**, except that *m*-xylene was used instead. Compounds **2**, **2′**, and **3** were synthesized under the reaction conditions that were the same as those of **1** and **1′**, except that 4-phenylpyridine (phpy) or pyridine was used instead. Compounds **1**–**3**, **1′** and **2′** are all stable to air and water.

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Keywords: dynamic conformations · macromolecular blocks · materials engineering · metal-organic nanotubes · supramolecular complexation

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[18] Crystal structure data for compound **1**: $C_{74}H_{52}N_6O_{30}Re_6$, $M_r = 2622.42$, Trigonal, $R\bar{3}$, $a = b = 21.7294(6)$ Å, $c = 13.5857(7)$ Å, $V = 5555.3(4)$ Å^3, $Z = 3$, $\rho_{calcd} = 2.352$ g cm^{-3}, $\mu = 9.860$ mm^{-1}, λ-(Mo-Kα) = 0.71073 Å, $F(000) = 3684$, $T = 150(2)$ K. Final *R indices*: $R1 = 0.0173$, $wR2 = 0.0456$ for 2093 reflections [$I > 2\sigma(I)$]; $R1 = 0.0185$, $wR2 = 0.0461$ for 2185 independent reflections (all data). For **1′**: $C_{66}H_{42}N_6O_{30}Re_6$, $M_r = 2516.26$, Trigonal, $R\bar{3}$, $a = b = 18.9203(3)$ Å, $c = 17.6307(7)$ Å, $V = 5465.8(2)$ Å^3, $Z = 3$, $\rho_{calcd} = 2.293$ g cm^{-3}. For **2**: $C_{98}H_{64}N_6O_{24}Re_6$, $M_r = 2826.75$, Trigonal, $R\bar{3}$, $a = b = 22.269(3)$ Å, $c = 14.957(5)$ Å, $V = 6424(2)$ Å^3, $Z = 3$, $\rho_{calcd} = 2.192$ g cm^{-3}. For **2′**: $C_{90}H_{54}N_6O_{24}Re_6$, $M_r = 2720.57$, Trigonal, $R\bar{3}$, $a = b = 22.0860(4)$ Å, $c = 15.0940(5)$ Å, $V = 6376.3(4)$ Å^3, $Z = 3$, $\rho_{calcd} = 2.126$ g cm^{-3}. For **3**: $C_{54}H_{30}N_6O_{24}Re_6$, $M_r = 2264.04$, Trigonal, $R\bar{3}$, $a = b = 21.234(2)$ Å, $c = 11.286(2)$ Å, $V = 4406.8(1)$ Å^3, $Z = 3$, $\rho_{calcd} = 2.559$ g cm^{-3}. CCDC 1424162 (**1**), 1424022 (**1′**), 1446494 (**2**), 1446106 (**2′**), and 1446297 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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