

Helical and polymeric nanostructures assembled from benzene tri- and tetracarboxylic acids associated with terpyridine copper(II) complexes

Pingshan Wang,^a Charles N. Moorefield,^b Matthew Panzer^c and George R. Newkome^{*ab}

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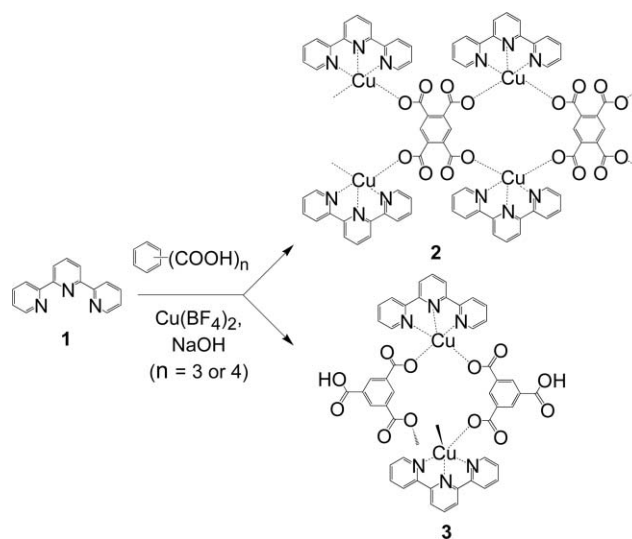
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A ladder-like framework was derived from benzene-1,2,4,5-tetracarboxylic acid with Cu^{II} and terpyridine; whereas with benzene-1,3,5-tricarboxylic acid, a helical structure was formed with two CO₂⁻ groups bridging opposing (terpyridine)Cu^{II} units and the other CO₂H connecting the helical cylinders *via* H-bonding.

Recently, inorganic and organic hybrids have focused on the dynamic aspects of crystal engineering,^{1–3} porous structures,⁴ and coordination polymers.⁵ Building blocks such as pyridine,⁶ bipyridine,^{7,8} and, to a lesser degree, terpyridine^{9,10} are often used to construct various molecular geometries, such as squares, tetrahedra and octahedra. With respect to architectural assemblies, terpyridine is an attractive component due to its ability to generate stable pseudo-octahedral dimers, under neutral conditions; as well, with carboxylate groups, terpyridines display versatile coordination properties with metals¹¹ forming well known chelate and bidentate structures. Lloret *et al.*¹² exploited these properties when they prepared a (terpyridine)Cu^{II} dinuclear complex bridged with either terephthalate or phthalate groups. To the best of our knowledge, there are no reports concerning the use benzene tri- and tetracarboxylic acids as components in terpyridine-based molecular lattices. Herein, we present our initial observations and results on the use of aromatic polycarboxylates as elements in terpyridine-based constructs.

An aqueous suspension (Scheme 1) of terpyridine **1**, 1 equiv. of Cu(BF₄)₂, 0.5 equiv. of 1,2,4,5-benzenetetracarboxylic acid, and 4 equiv. of sodium hydroxide was heated at 90 °C for 5 h to give a translucent blue–green solution, which after 48 h at 25 °C afforded (90%) **2** as green single crystals.†‡ X-Ray diffraction analysis (–100 °C) of **2** revealed that the crystal lattice exhibited a staircase- or ladder-like structure, shown in Fig. 1. The tetracarboxylate functions as a connector to align opposing, planar (terpyridine)Cu^{II} complexes, in a stacked manner, *via* 1,2- and 4,5-coordination. The O–Cu distances within the lattice differ by 0.283 Å with the 1- and 4-carboxylate O–Cu bond length being longer (2.221 Å) than the corresponding 2- and 5-carboxylate O–Cu bond length (1.938 Å). The Cu···Cu distances in the vertical and horizontal planes were observed to be 7.722 and 6.656 Å, respectively. The terpyridine plane is positioned at an angle of 25.54° with respect to the plane of the benzene ring. Adjacent ‘ladders’ reveal a short distance (3.862 Å) between terpyridine planes suggesting π–π interactions.

Thus, employing benzene-1,3,5-tricarboxylic acid, as the connective element, under similar reaction conditions, gave (88%) X-ray quality green crystals,†‡ which revealed a motif with an



Scheme 1 Chemical structures of the repeat units in the ladder-like and helical assemblies **2** and **3**.

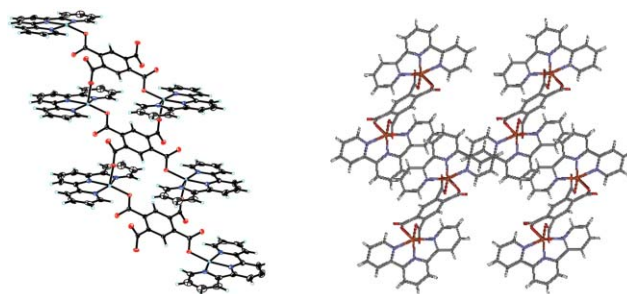


Fig. 1 Ladder-like structure of neutral molecule **2**. Left: Side view of the packing in the structure; red atoms: O; blue atoms: Cu; green atoms: N. Right: Top view of the crystal packing of **2**.

empirical formula of C₄₈H₃₆Cu₂N₆O₁₅ and an unexpected helical structure^{13–15} (Fig. 2). With respect to the tricarboxylate component, two of the three carboxylic acids are deprotonated and coordinated with opposing (terpyridine)Cu^{II} complexes, while the remaining COOH moiety is oriented longitudinally (*y*-axis) facilitating the H-bonding that promotes the helix formation.¹⁶ The resultant helical channel,⁵ possessing a 6.276 Å diameter and three water molecules, is held together by H-bonding to the complexed carboxylates. Each helical cylinder unit is thus connected by H-bonding of the water molecules and *y*-axis carboxylic acids facilitating the construction of the 3D framework.

*newkome@uakron.edu

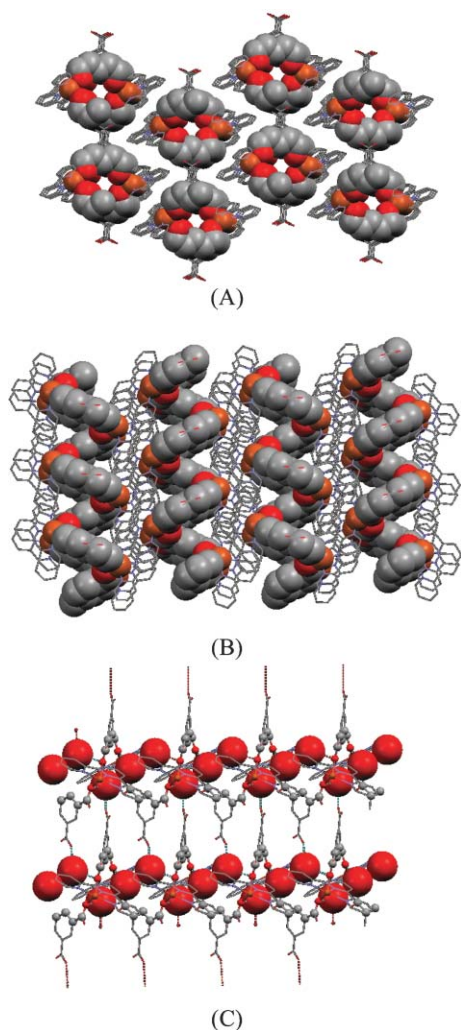


Fig. 2 Crystal packing illustration of the helical structure of **3**. (A) Space-filling top view; (B) Space-filling side view and (C) a view of the included water molecules (red spheres) that occupy the channels of the helices.

(Fig. 2(A) and (C)). The O–Cu distances are observed to be 1.950 and 2.180 Å, while the Cu···Cu distances to its two nearest neighbors are 7.861 and 8.067 Å. Along the *x*-axis (Fig. 3), the short distance contacts (3.342 Å) suggest π – π stacking between the

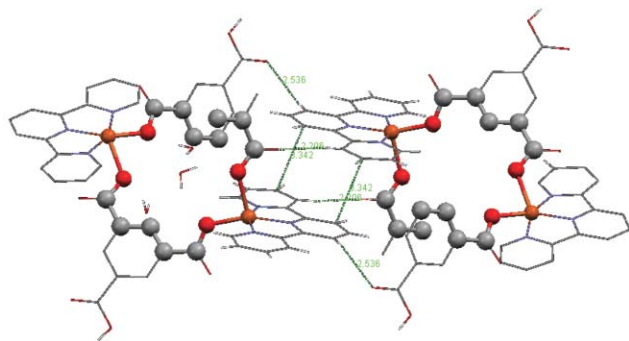


Fig. 3 Side-by-side helical units of the neutral molecule **3** reveal the short distance contacts between the terpyridine protons and the carboxylate carbonyl oxygens (hydrogens and H-bonding omitted for clarity).

terpyridine planes. Notably, the protons in the terpyridine plane are more acidic after complexation with Cu^{II}. The extremely short distance (2.2206 Å) for the unbonded O₂–H₁₂(tpy) suggests a strong interaction between the two opposing helical structures; also the short distance (2.536 Å) for the unbonded O₁₂–H₇(tpy) provides a potential explanation for the formation of the 3D structure along the *x*-axis.

TGA studies indicated that the crystalline **3** loses the encapsulated water molecules at 93–110 °C; this is a 5% weight loss compared with the theoretical value of 5.07% for total dehydration. The crystals were virtually unchanged (0.54 wt% loss) until 276 °C; whereupon, decomposition occurred.

In summary, benzenepolycarboxylic acids have been found to promote the construction of (terpyridine)Cu^{II}-based ladder-like and helical architectures. In both cases, carboxylates function as bridging units for two complexed terpyridines. This strategy is currently being applied to other functionally-modified terpyridine building blocks in order to expand this promising method for the controlled construction of new multi-dimensional networks. Variation of the carboxylic acid elements along with the polypyridinyl complexes is envisioned to produce new porous materials, which could find potential applications in self-assembled nanoscale molecular devices and photoactive molecular-scale wires.

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Pingshan Wang,^a Charles N. Moorefield,^b Matthew Panzer^c and George R. Newkome^{*ab}

^aDepartments of Polymer Science and Chemistry, The University of Akron, Akron, OH 44325-4717, USA

^bMaurice Morton Institute for Polymer Science, The University of Akron, Akron, OH 44325-4717, USA

^cDepartment of Chemistry, The University of Akron, Akron, OH 44325-4717, USA. www.dendrimers.com;

E-mail: newkome@uakron.edu; Fax: +1 330 972 2413;

Tel: +1 330 972 6458

Notes and references

† *Preparations*: **2**: A mixture of terpyridine (10 mg, 43 μmol), 1,2,4,5-benzenetetracarboxylic acid (5.45 mg, 21.4 μmol), Cu(BF₄)₂·4H₂O (13.25 mg, 43 μmol) and NaOH (3.5 mg, 8.75 mmol) in deionised water (8 ml) were sonicated for 30 min, then the greenish blue solution was heated at 90 °C for 12 h. Light-green crystals were collected (90%) after cooling the solution to 25 °C and standing for 2 days. **3**: A similar procedure to preparing **2** was used to obtain the green crystals (88%), except for the substitution of 1,3,5-benzenetricarboxylic acid and the use of 3 equiv. of NaOH.

‡ *Crystal data*: for **2**: C₄₀H₂₄Cu₂N₆O₈, *M* = 843.73, green prism, 0.13 × 0.08 × 0.04 mm, triclinic, space group *P* $\bar{1}$, *a* = 7.722(2), *b* = 10.082(3), *c* = 12.348(3) Å, β = 104.207(5)°, *V* = 899.7(4) Å³, *Z* = 1, *D*_c = 1.557 Mg m⁻³, *F*(000) = 428, *T* = 1.75–28.35°, 7951 reflections collected, 4138 unique (*R*_{int} = 0.0419), *R*1 = 0.0560, *wR*2 = 0.1148, Final *R* indices [*I* > 2σ(*I*)], data/restraints/parameters = 4138/0/254. For **3**: C₄₈H₃₆Cu₂N₆O₁₅, *M* = 1063.91, green prism, 0.18 × 0.15 × 0.08 mm, triclinic, space group *P* $\bar{1}$, *a* = 7.8605(8), *b* = 11.7030(11), *c* = 22.549(2) Å, β = 89.118(2)°, *V* = 2070.7(4) Å³, *Z* = 2, *D*_c = 1.706 Mg m⁻³, *F*(000) = 1088, *T* = 1.74–28.31°, 18712 reflections collected, 9660 unique (*R*_{int} = 0.0289), *R*1 = 0.0409, *wR*2 = 0.0910, Final *R* indices [*I* > 2σ(*I*)], data/restraints/parameters = 9660/0/748. CCDC 246958 and 246959. See <http://>

www.rsc.org/suppdata/cc/b4/b412055h/ for crystallographic data in .cif or other electronic format.

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