

A metal–organic framework replete with ordered donor–acceptor catenanes†

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A metal–organic framework was constructed from struts in which donor–acceptor [2]catenane units become integrated, leading to a high density of these molecular machinery modules positioned precisely in well-defined layered (2D) structures.

Mechanically interlocked molecules, such as bistable catenanes and rotaxanes¹ have been used as intrinsically switchable components in molecular electronic devices² and nanoelectromechanical systems³ in the form of molecular shuttles⁴ and switches.⁵ The performance of these devices is highly dependent on our ability to place them in a precise location and orientation,⁶ with high coverage on a surface,⁷ and with reproducibility of action.^{3–5} We sought to overcome these challenges by attaching the active molecules covalently onto the organic links of metal–organic frameworks (MOFs).⁸ In this way, the MOF backbone—metal-oxide joints⁹ and organic struts—could be viewed as a platform onto which active molecules may be precisely attached.¹⁰ Although MOFs having rotaxanes and pseudorotaxanes as links have been reported,¹¹ catenane-MOFs remain unknown, presumably because of the crystallization challenge presented by the sheer size, flexibility, and asymmetry of the strut. Here, we report the successful synthesis and crystal structure of MOF-1011 in which a bulge-shaped strut BPP34C10DC-CAT is linked to a trigonal Cu(I) unit to give (Fig. 1) a two-dimensional arrangement based on the **sql** topology.¹² This structure is replete with ordered catenanes (one per copper unit, eight per unit cell, and eighty-one per 100 nm² surface) throughout the crystal.

Single crystals of Cu(BPP34C10DC-CAT)(NO₃)₃ (MOF-1011) were obtained by heating H₂BPP34C10DC-CAT (Fig. 1a) and Cu(NO₃)₂·2.5H₂O in a mixture of *N,N*-dimethylformamide (DMF), EtOH, and H₂O. Here, H₂BPP34C10DC-CAT was synthesized by using a bis-carboxylic acid containing bis-*p*-phenylene[34]-crown-10 (BPP34C10)¹³ to assist the formation of a mechanically interlocking tetracationic cyclophane

cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺)¹⁴ by clipping the 1,1'-[1,4-phenylenebis(methylene)bis(4,4'-bipyridinium) dication with 1,4-bis(bromomethyl)benzene around the π -electron-rich hydroquinone unit of the crown ether.¹³ The single crystal structure of BPP34C10DC-CAT (Fig. 1b), the ester form of H₂BPP34C10DC-CAT, provided direct evidence for the formation of the mechanically interlocked structure. The strut is 19.3 Å in length (distance between the two carboxylate carbon atoms) with apparent bending in the linear strut (the deviations of two C–C≡C–C dihedral angles are 9.2° and 5.7°, respectively), a phenomenon commonly observed¹⁵ in strained large conjugated π -systems containing acetylenic bonds. In this bulge-shaped strut (Fig. 1c), the farthest atom in the catenane unit is 13.5 Å away from the organic backbone. This strut,[§] with a molecular weight of 1779.46 g mol⁻¹, includes an unprecedented 100 non-hydrogen atoms, excluding anions, making it possibly the most complicated linker ever exploited successfully in MOF synthesis.

Single-crystal X-ray diffraction reveals that MOF-1011¶ (Fig. 1d) has a 2D layer structure. Cu(II) is reduced to Cu(I) during the reaction, resulting in electron paramagnetic resonance (EPR) silence in the product. Each Cu⁺ ion is bonded to two carboxylate groups from two BPP34C10DC-CAT and to one acetylenic bond from a third BPP34C10DC-CAT in an η^2 fashion, a coordination geometry also observed¹⁶ in discrete π -alkyne copper(I) complexes. Interestingly, only one acetylenic unit from each organic strut is coordinated to Cu(I), making the strut more bent within the 2D layer (bend angles are *ca.* 55° and 64°, respectively, for two struts in the asymmetric unit in the unit cell) and asymmetric. The trigonal units Cu⁺ and the backbones of BPP34C10DC-CAT are articulated into a 2D network. The smallest repeating grid in this 2D network is composed of 44 non-hydrogen atoms (36 C, 4 O and 4 Cu). Mechanically interlocked BPP34C10 (34-membered polyether ring) and CBPQT⁴⁺ (28-membered cyclophane) are arranged so that they are alternating up-and-down throughout the 2D layer (Fig. 1e). These mechanically interlocked components are chemically bonded to the 2D net by sharing hydroquinone rings with the backbones. Each 44-membered grid in a 2D sheet shares six atoms with two [2]catenanes.

The layers are packed along the *b*-axis in an eclipsed geometry, with a distance of 13.6 Å between every two interdigitated sheets (Fig. 2). Noncovalent bonding interactions between the crown ethers and CBPQT⁴⁺ are sustained upon the formation of the relatively stronger Cu–O and Cu–C bonds. Further investigation of the crystal structure of

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MOF-1011 reveals that the distance between the bipyridinium rings and the hydroquinone units is 3.4 Å, 0.2 Å less than that present in the single molecule model BPP34C10DE-CAT, which suggests enhanced π - π stacking interactions caused by the layered extended structure. We have noted that the (*R*) and (*S*) enantiomers of the struts are present in a 1 : 1 ratio in the crystal structure of MOF-1011, in which the bipyridinium rings in the CBPQT⁴⁺ cyclophane are arranged in the same

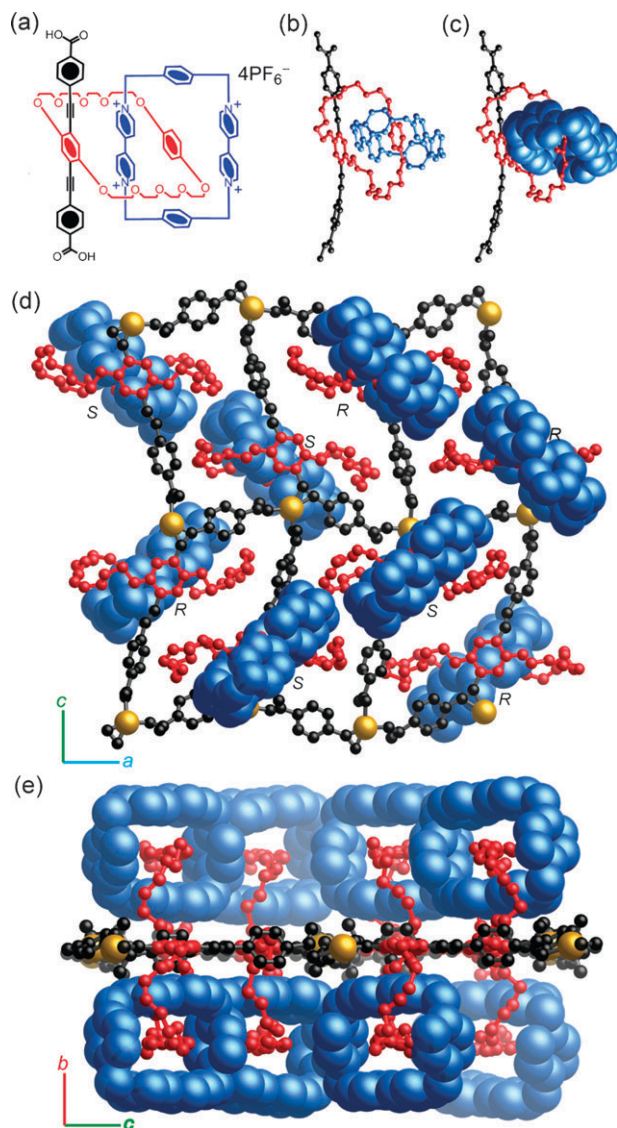


Fig. 1 (a) Structure formula for H₂BPP34C10DC-CAT. (b) Ball-and-stick representation of the solid-state structure of BPP34C10DE-CAT. The strut is bent as a result of the steric hindrance from the interlocked rings. The CBPQT⁴⁺ ring is aligned *ca.* 75° with respect to the linear strut. (c) Mixed ball-and-stick and space-filling representation of the bulge-shaped BPP34C10DE-CAT. (d) Plan view of MOF-1011 along the *b*-axis. The planar chirality of each catenane substructure is labeled either (*R*) or (*S*). (e) Side-on view of MOF-1011 along the *a*-axis. The [2]catenane substructures are positioned equally on both sides of each layer. Cu, gold; crown ethers, red; CBPQT⁴⁺, blue; organic struts, black. In (d) and (e), the CBPQT⁴⁺ rings are illustrated in space-filling format while other atoms are portrayed with a ball-and-stick representation. All hydrogen atoms and anions have been omitted for clarity.

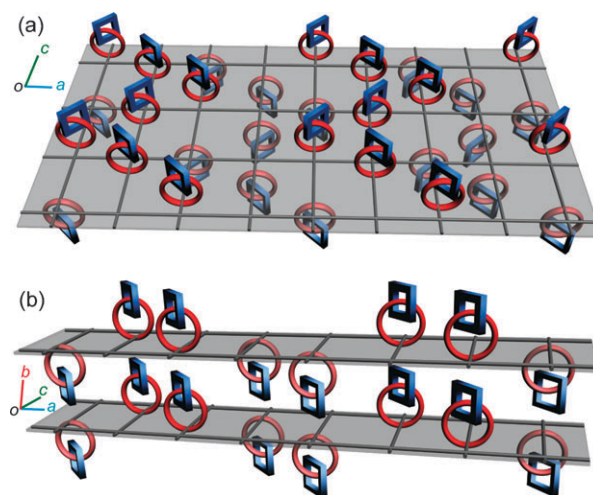


Fig. 2 (a) Schematic view of MOF-1011 layer structure. Copper and the backbones of the struts are articulated into the layered structure based on *sql* topology, shown in the layer with grey grids identifying the struts to which the catenanes are fused. The [2]catenane substructures are chemically bonded to the backbone grids along the *c* direction on both sides of each layer following zigzag patterns. (b) The layers are packed along the *b*-axis in an eclipsed geometry, with two neighboring layers shown. Catenanes from two neighboring layers interdigitate each other along the *a*-axis. The CBPQT⁴⁺ rings from both layers are aligned in an alternating fashion. Color code: MOF-1011 backbone, grey layer with black struts; BPP34C10, red rings; CBPQT⁴⁺, blue squares.

direction with respect to the linear backbone, an orientation different from the crystal structure of BPP34C10DE-CAT, where the CBPQT⁴⁺ cyclophane is aligned *ca.* 75° with respect to the linear strut. This co-conformational change may be caused by the increased crowding between each neighboring layer. MOF-1011 exhibits unprecedented ordering of [2]catenanes in an extended solid structure. Compared to other strategies for anchoring mechanically interlocked components on surfaces,^{7,17} a higher coverage density of [2]catenanes was achieved in MOF-1011. Eighty-one [2]catenanes are precisely and chemically bonded on two sides of every 100 nm² backbone net, which shows a high level of uniformity and long-range ordering of catenanes compared to chemisorbed layers or physisorbed layers of catenanes on surfaces. The powder X-ray diffraction pattern† of the MOF-1011 bulk material matches the simulated pattern from the crystal structure. The purity of the MOF-1011 was further confirmed by elemental analysis.†

In conclusion, we have incorporated donor–acceptor [2]catenanes successfully into a solid-state 2D network. The synthesis of MOF-1011 not only represents an entirely new approach to anchoring components of prototypical molecular machines into solids that is quite different from any previously established methods, but it also ensures higher accessibility and processability compared to 3D bulk materials. This structure demonstrates the first step towards the construction of new synthetic materials with comprehensive parallel functions. Incorporating dynamic behavior into robust crystalline scaffolds in a highly controllable fashion would reach the desired complexity.

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Notes and references

§ The CBPQT⁴⁺ ring, a π -electron deficient cyclophane, is tightly catenated by the crown ether macrocycle as the consequence of multiple [C–H...O], [C–H... π] and [π ... π] stacking interactions.¹⁸ Interestingly, the [2]catenane is endowed with planar chirality¹⁹ induced within the crown ether since free rotation of the strut is prohibited around the tetrasubstituted hydroquinone ring on the account of the BPP34C10 ring being catenated by the CBPQT⁴⁺ ring. Equal numbers of molecules with (*R*) and (*S*) chiralities were identified in the crystal structure, rendering crystals racemic overall.

¶ Crystal data for MOF-1011 after SQUEEZE: C₁₆₄H₁₅₆Cu₂N₈O₂₈, *M_r* = 2814.05, orthorhombic, space group *Pca*2₁, *a* = 30.5784(10), *b* = 13.5840(4), *c* = 32.0739(8) Å, *V* = 16808.3(8) Å³, *D_c* = 1.112 g cm⁻³, λ = 1.54178 Å, *Z* = 4, *R*₁ [*I* > 2 σ (*I*)] = 0.1976, *wR*₂ (all data) = 0.4854, GOF = 1.829. The various geometrical restraints were used involving some atoms of the crown ether moiety. Benzene rings were refined as perfect hexagons to minimize the number of refined parameters. Assignment and refinement of the structure proved the formation of the catenane-MOF.

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