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Application of a tetrapyrimidyl cyclobutane synthesized in the organic solid state: a halogen-bonded supramolecular ladder†

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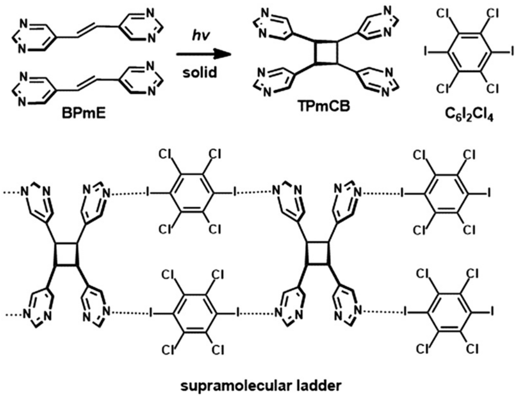
A halogen-bonded supramolecular ladder comprised of a novel pyrimidine-based cyclobutane photoproduct synthesized in the organic solid state *via* a [2 + 2] photoreaction is reported. The photoproduct *rctt*-tetrakis(5′-pyrimidyl)cyclobutane functions as rungs while the linear divergent halogen-bond donor 1,4-diiodoperchlorobenzene acts as the rails. Our report also confirms the structure and stereochemistry of the tetrapyrimidyl cyclobutane ring system.

The formation of organic networks continues to be an active area of research for materials scientists and crystal engineers. Diversifying the geometry of molecular nodes and linkers continues to afford network solids of varied topologies.[1] An approach that can instill diversity into these solids is based upon the modularity of the components. Recently, the ability of tetrafunctional *rctt*-tetrakis(4-pyridyl)cyclobutane, a photoproduct generated in the organic solid state, to form both a square lattice[2] and a diamondoid net[3] has been reported by the simple variation of the halogen-bond donor. In particular, the square lattice was realized when the cyclobutane is combined with 1,4-diiodoperfluorobenzene while the isosteric donor 1,4-diiodoperchlorobenzene (**$C_6I_2Cl_4$**) yielded a diamondoid net.

Cyclobutane-based products generated in the solid state are ideal building blocks to investigate modularity of these networks within organic solids. Since, the pendant groups attached to the cyclobutane ring system can be modified based on substituents attached to the central carbon–carbon double (C═C) bond before photoreaction.[4] To date, all cyclobutane-based molecules synthesized in the solid state that have been used deliberately as building blocks to form extended organic networks have possessed *n*-pyridyl substituents as linker groups.[5] It stands to reason that extending the solid-state reactivity to cyclobutane rings lined with other heterocycles could significantly expand the scope of using this chemistry for network design and discovery.

Here, we report the application of the tetrafunctional photoproduct *rctt*-tetrakis(5′-pyrimidyl)cyclobutane (**TPmCB**) as a molecular building block that supports a halogen-bonded supramolecular ladder (Scheme 1). One of us has reported that *trans*-1,2-bis(5′-pyrimidyl)ethylene (**BPmE**) is photoactive and undergoes a [2 + 2] cycloaddition reaction in the solid state as a pure solid to yield a cyclobutane product.[6] The product is, thus, generated without assistance of auxiliary molecules (*e.g.* ditopic templates) and reacts quantitatively and without side products. The stereochemistry of the photoproduct remained, however, unassigned yet based on the structure of crystalline **BPmE** would be expected as **TPmCB**. In addition to now confirming the stereochemistry of the novel tetra(pyrimidyl)cyclobutane photoproduct, we



Scheme 1 [2 + 2] cycloaddition reaction to form **TPmCB** in the organic solid state and the resulting supramolecular ladder held together by halogen bonds from $C_6I_2Cl_4$.

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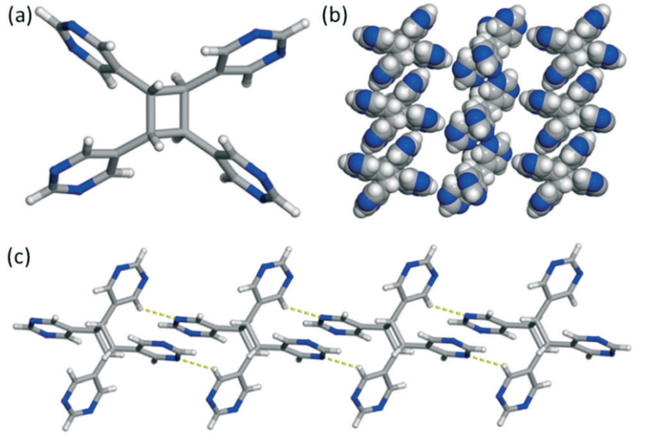

Fig. 1 X-ray crystal structure of **TPmCB**: (a) view of *rctt* stereochemistry of the cylcobutane ring, (b) face-to-face π–π stacking of the pyrimidyl rings, and (c) C–H⋯N hydrogen bonds of the extended solid (yellow dashes = hydrogen bonds). The disorder in **TPmCB** was removed for clarity.

also show that co-crystallization of **TPmCB** with the *exo*-divergent halogen-bond donor $C_6I_2Cl_4$ results in a supramolecular ladder wherein **TPmCB** and $C_6I_2Cl_4$ act as the rungs and rails, respectively. While supramolecular ladders have been formed using hydrogen bonds and coordination chemistry, there are only a limited number of supramolecular ladders sustained by halogen bonds.[7] To the best of our knowledge, this is the first reported co-crystal based upon a tetrafunctional photoproduct based upon the pyrimidyl ring system. Our work, thus, expands the diversity of photoproducts generated by the solid-state synthesis approach. The ladder reported here hosts toluene molecules in the form of (**TPmCB**)·2($C_6I_2Cl_4$)·(toluene) (**1**).

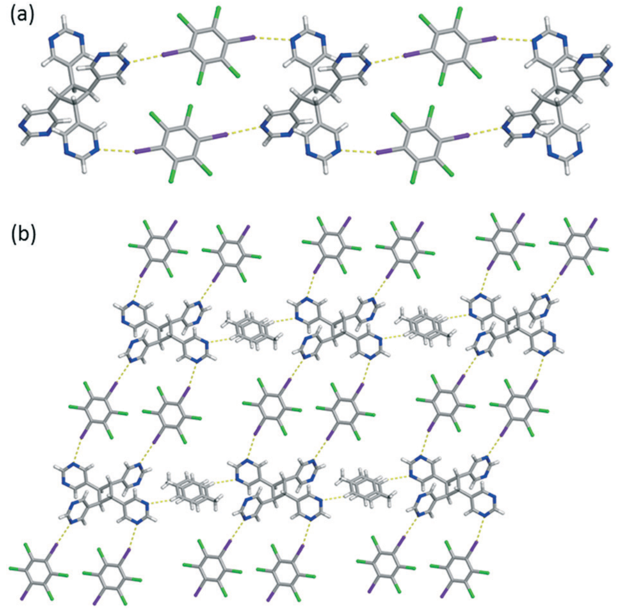

Fig. 2 X-ray structure of **1**: (a) illustrating the supramolecular ladder and (b) the two-dimensional sheets of **1** (yellow dashes = halogen and hydrogen bonds).

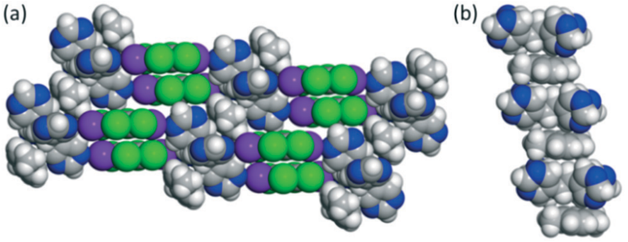

Fig. 3 X-ray structure of **1**: (a) illustrating C–H⋯π interaction between **TPmCB** and the included toluene molecule and (b) a closer view of the infinite stacking of the components.

The components of the ladder of **1** are not commercially available and were synthesized as reported.[6,8] The tetra(pyrimidyl)photoproduct was generated in near quantitative yield by exposing UV light (medium-pressure Hg lamp) to a powdered sample of **BPmE** in a period of 20 hours (Fig. S1†). The resulting solid was used directly following the photoreaction. Single crystals of **TPmCB** (25.0 mg) in the form of plates suitable for single-crystal X-ray diffraction were generated by dissolution and slow evaporation from ethanol (3.0 mL).

The cyclobutane crystallizes in the monoclinic space group *C*2/*c*. The asymmetric unit contains one half of a molecule of **TPmCB** that sits on a centre of inversion. The stereochemistry of the cyclobutane is confirmed as the *rctt*-isomer (Fig. 1a). In the arrangement, **TPmCB**, which is disordered over two sites (site occupancies: 0.89 and 0.11), is sustained *via* face-to-face π–π stacking (3.67 Å) and C–H⋯N hydrogen bonds [C⋯N 3.662(4) Å; C–H⋯N 160.57(16)°] of the pendant pyrimidyl rings (Fig. 1b and c).

A supramolecular ladder forms when **TPmCB** is co-crystallized with $C_6I_2Cl_4$. Single crystals of **1** in the form of blocks were realized upon slow evaporation by combining an ethanol (2.0 mL) and toluene (1.0 mL) solution of **TPmCB** (25.0 mg) and a warm toluene (2.0 mL) solution of $C_6I_2Cl_4$ (63.5 mg) (1 : 2 molar ratio).

The components of **1** crystallize in the triclinic space group $P\bar{1}$. The asymmetric unit contains one half of a molecule of **TPmCB**, one molecule of $C_6I_2Cl_4$, and a disordered toluene molecule that resides on a centre of inversion. Each pyrimidyl ring participates in a single I⋯N halogen bond with $C_6I_2Cl_4$ [I⋯N 2.865(2) and 2.991(2) Å; C–I⋯N 177.44(8) and 165.49(9)°] to afford a supramolecular ladder (Fig. 2a).[9] **TPmCB**, thus, acts as a 4-connected node that serves as the rungs while $C_6I_2Cl_4$ serves as the rails. In addition, **TPmCB** acts as an H-shaped building block to form the ladder.[10]

The formation of the supramolecular ladder does not require each N-atom of **TPmCB** to participate in a halogen bond. Moreover, two of the remaining N-atoms are engaged in a C–H⋯N interactions [C⋯N 3.467(7) Å; C–H⋯N 155.4(5)°] with the *ortho*-hydrogen on the included toluene. The interaction results in the formation of a two-dimensional sheet (Fig. 2b). Thus, each cyclobutane is engaged in four

I···N halogen bonds and two C–H···N hydrogen bonds. The sheets stack with the included toluene molecules sandwiched between nearest-neighbouring cyclobutane rings. The four-membered ring participates in C–H···π interactions with the aromatic solvent (Fig. 3a). The interactions are manifested as infinite columns running along the crystallographic *a*-axis (Fig. 3b).

Conclusions

We have utilized the solid state to generate a cyclobutane-based building block in the form of **TPmCB** that yields a supramolecular ladder when co-crystallized with **$C_6I_2Cl_4$**. The components self-assemble *via* halogen bonds with the photoproduct acting as H-shaped nodes of the ladder. Overall, the **TPmCB** acts as the rungs while **$C_6I_2Cl_4$** acts as the rails. Currently, we are attempting to incorporate **TPmCB** into other organic solids, as well as metal–organic materials, and expand the inclusion properties of this emerging class of pyrimidyl-based solids.

Conflicts of interest

There are no conflicts to declare.

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