

A supramolecular 2:1 guanidinium-carboxylate based building block for generation of water channels and clusters in organic materials

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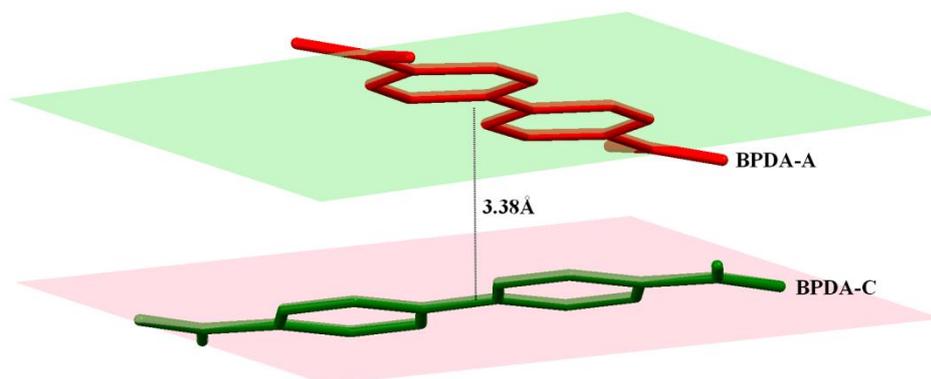
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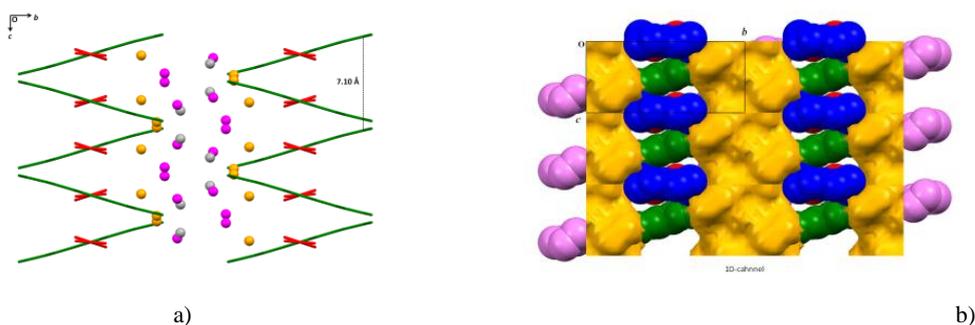
[1] Crystal Packing Details of crystal type I

Figure S1: Cross-motif in crystal type I.



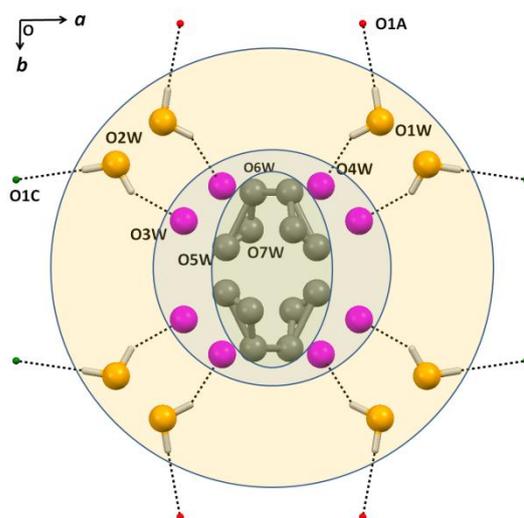
Enlarged view of the cross-motif in crystal type I. Two independent **BPDA** units are assembled in a crossed manner with respect to one another. The planes of molecules **BPDA-A** (red) and **BPDA-C** (green) are separated from one another by the distance 3.38 Å. The carboxylate group of **BPDA-A** is slightly twisted, while carboxylate of **BPDA-C** is co-planar with respect to the bipyridine planes.

Figure S2: The crystal packing of type I, viewed along the *a*-axis.



- a) Side view of the crystal type I (along the *a*-axis), all **BPDA-A** (coloured in red) and **BPDA-C** (coloured in green) molecules are shown in a capped sticks model. The **BPDA** molecules are arranged in a zigzag order and generate one-dimensional water channels. The water molecules in the channel are shown as different coloured spheres (orange, magenta and grey). The hydrogen atoms and **TBD** molecules are omitted for the clarity.
- b) Space fill representation of Crystal type I viewed along the *a*-axis. The orange coloured 1D helical column show the space occupied by water molecules (**BPDA-A**: red, **TBD-B**: blue, **BPDA-C**: green, **TBD-D**: pink).

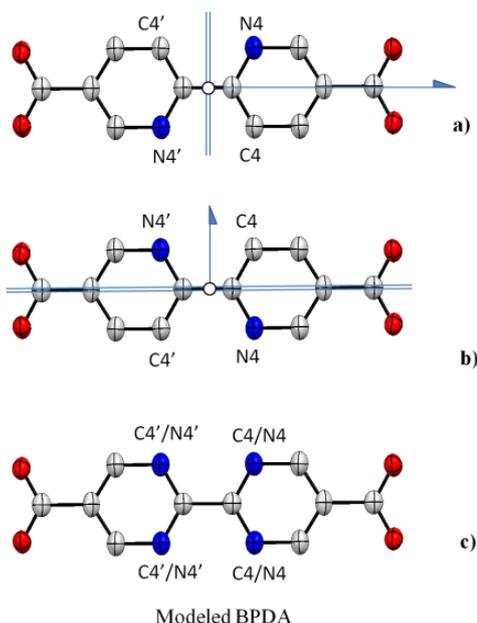
Figure S3: A water channel in crystal type **I**, viewed along the *c*-axis and model of disordered water molecules.



An enlarged view of a 1D water channel with three hydration shells viewed along the *c*-axis. Water molecules O1W and O2W (coloured in orange) belong to the first hydration shell and are anchored to the O1A and O1C of BPDA-carboxylates by H-bonding. The middle shell water molecules O3W and O4W (coloured in magenta) interact with water molecules O2W and O1W, respectively. The electron density of the third hydration shell, constituting the core of the channel has been modeled by three positions O5W-O7W (coloured in grey), with occupancies 0.371(8), 0.101(6), 0.236(8), respectively. The H-atoms of O3W-O7W could not be located in the electron density map.

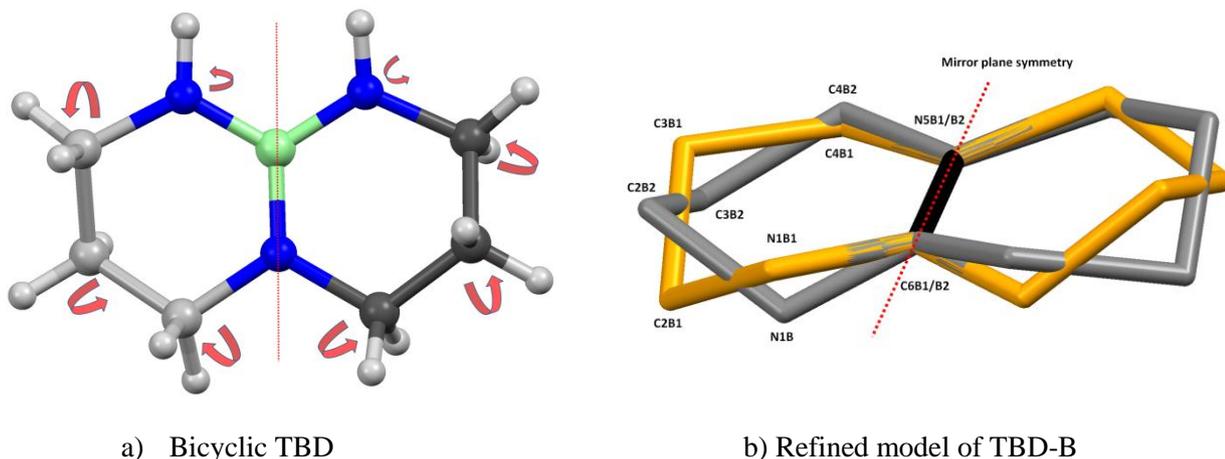
[2] Refinement of structural disorders in crystal type I

Figure S4: Refinement model of (2,2'-Bipyridine-5,5'-dicarboxylic acid, **BPDA**) in crystal type I



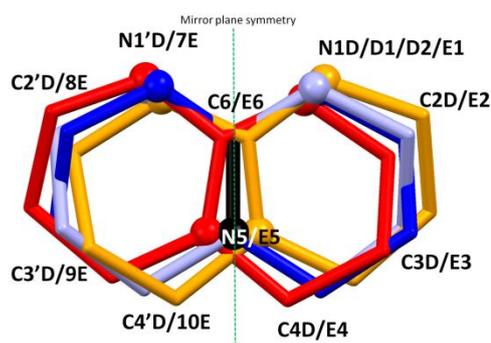
The pyridine rings of **BPDA** are co-planar and disordered at the nitrogen/carbon sites because of the mirror planes and rotation axes in the space group *Pmna*, shown here as double lines and arrows, respectively in a) and b) with small black circles indicating inversion centers. In the refinement the N4 and C4 atoms were restricted to have similar positions and anisotropic displacement parameters (Fig. c) with occupancy ratios 0.50.

Figure S5: Refinement of molecule **TBD-B** in crystal type I



- The **TBD-B** molecule is a fused bicyclic ten-membered heterocycle. These rings are non-planar and flexible (the movement of atoms is shown by red colour curved arrows).
- The molecule **TBD-B** is located on mirror plane and two alternative ring pucker modes of each side of the mirror plane gives two alternative molecular conformations shown in grey and orange. The C-C and C-N distances were restrained to 1.512 (4) Å and 1.333(3)-1.463(5) Å respectively (C-N bond length varies according to double bond and single bond characters due to delocalization of π -electron cloud). For clarity H-atoms are omitted.

Figure S6: Refinement of molecule **TBD-D** in crystal type **I**



The molecule TBD-D adopts four different orientations exhibiting conformational as well as positional disorder due to its ring puckering and amidine delocalization of π -electron system. These disorders were modeled using four sets of atomic sites designed as original site (D, light blue) and alternative sites D1(red), D2(blue) and E(orange) with occupancies 0.329 (11), 0.329 (11) and 0.168 (11) respectively. The C-C and C-N distance of disordered orientations were restrained to 1.512 Å and 1.333-1.463 Å respectively (the bond length variation in amidine (N=C-N) group of TBD from single bond-double bond character due to delocalization of π -electron cloud). Hydrogen atoms are omitted for clarity.