

Supplementary Material (ESI) for Chemical Communications

**Molecular encapsulation of a discrete water of (H<sub>2</sub>O)<sub>32</sub> cluster with S<sub>6</sub> symmetry in an organic crystalline supermolecule**

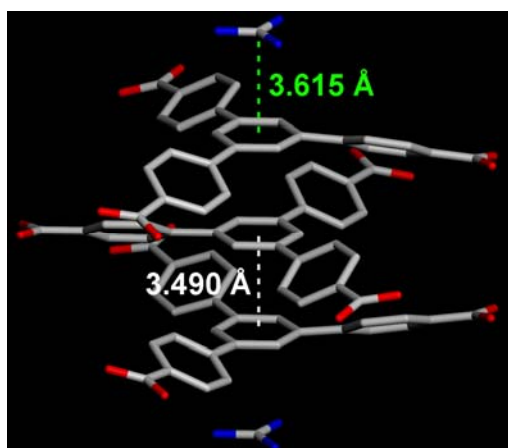
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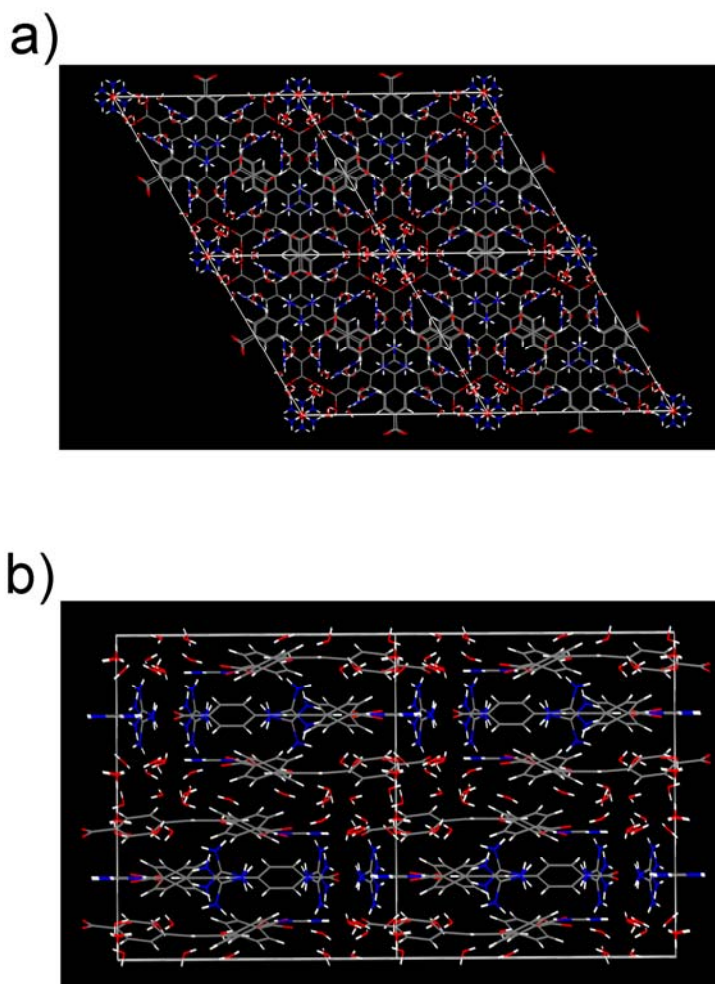
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**Electronic Supplementary Information**

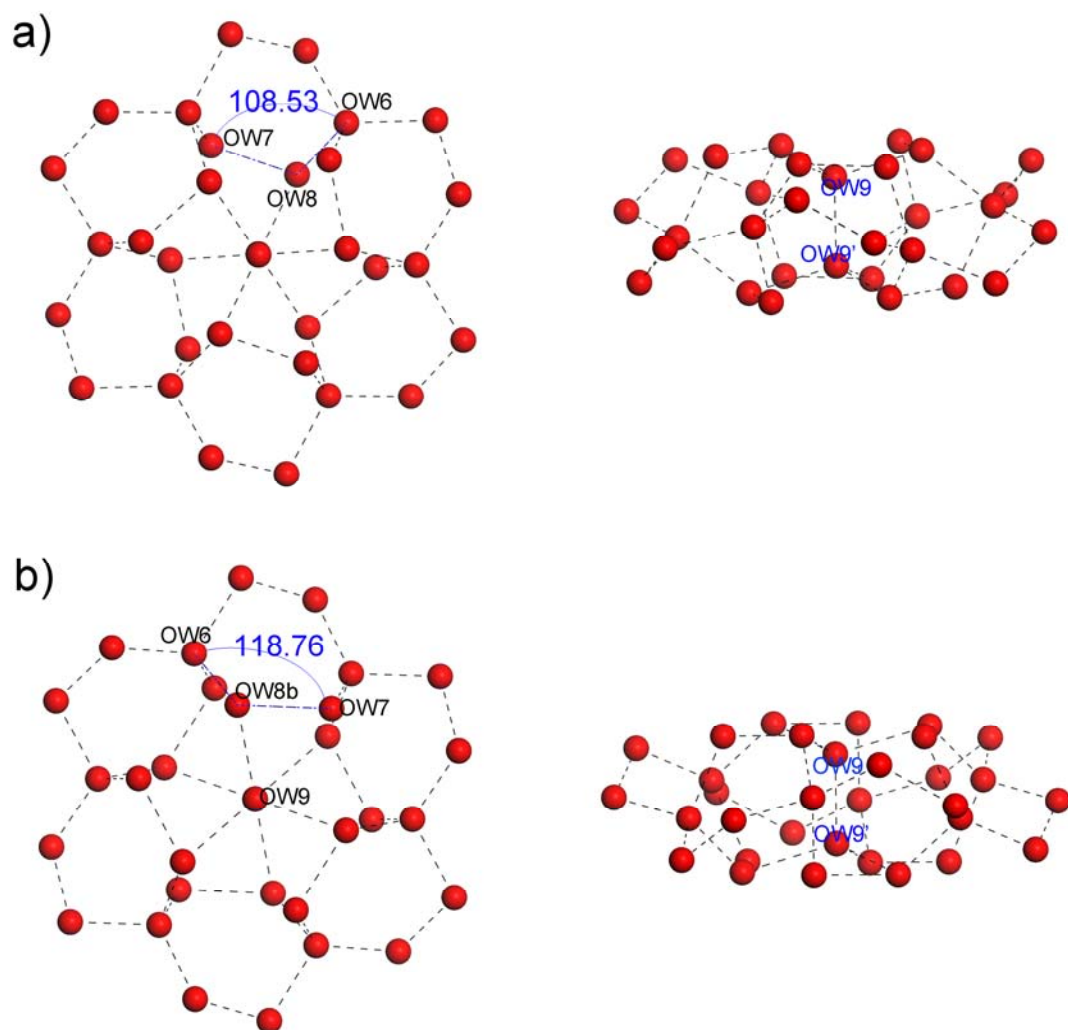
**Figure S1-S3**



**Fig. S1** Side view of the stacking of adjacent three BTBs shown in Fig. 2b with two guanidiniums above and below. All molecules are shown in a stick model and the hydrogen atoms are omitted for the clarity. Red: O; blue: N; gray: C.



**Fig. S2** 3D structure of **1** a) along the *c*-axis; b) along the *a*-axis. Red: O; blue: N; gray: C; White H.



**Fig. S3** Two 3D structures of  $(\text{H}_2\text{O})_{32}$  clusters due to the disorder of OW8. a) OW8; b) OW8b. The Ow6-Ow8-Ow7 angel and OW6-Ow8b-Ow7 angel were shown in blue. The black dash lines indicate the hydrogen between two oxygen atoms. Left: top view; right: side view.