Supporting Information

Structural refinement:

For the structures after irradiation, all non-hydrogen atoms of the product were located in Fourier difference maps, calculated with coefficients F_o(*exposed*)-F_o(*pre-exposure*), and then refined with restraints and constraints of the geometrical and thermal parameters of the reactant and product atoms bond lengths and thermal parameters (SADI and EADP instructions of *SHELXL*-97). For example, in the SHELX input file, (only) the following restraints and constraints commands have been used:

....

EADP O9 O9B

EADP O10 O10B

EADP C41 C41B

EADP C42 C42B

EADP C43 C43B

EADP C44 C44B

EADP C45 C45B

SADI C41 O9 C41B O9B

SADI C41 O10 C41B O10B

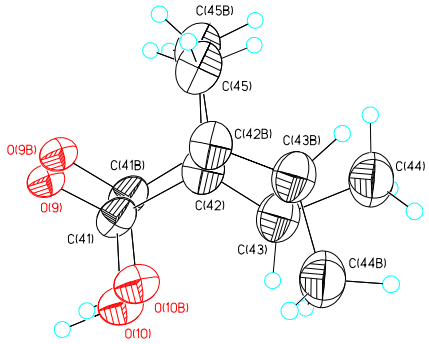
SADI C41 C42 C41B C42B

SADI C42 C43 C42B C43B

SADI C43 C44 C43B C44B

SADI C42 C45 C42B C45B

....



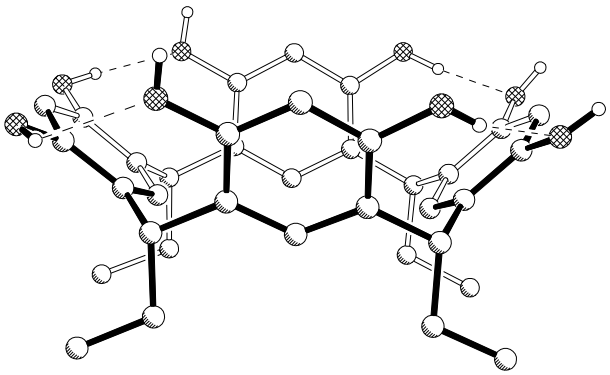
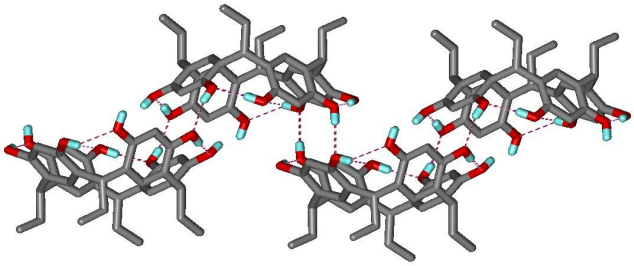
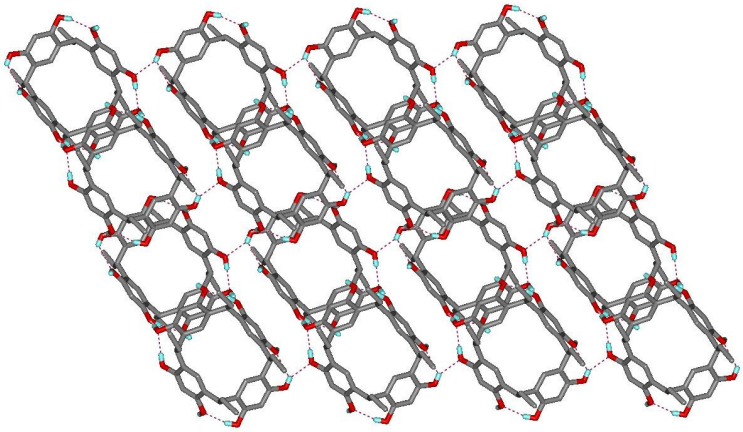


Figure S1: CECR with intramolecular hydrogen bond connectivity of C_s symmetry.



(a)



(b)

Figure S2. The hydrogen-bonded layer in **1** viewed (a) from the side and (b) from above.

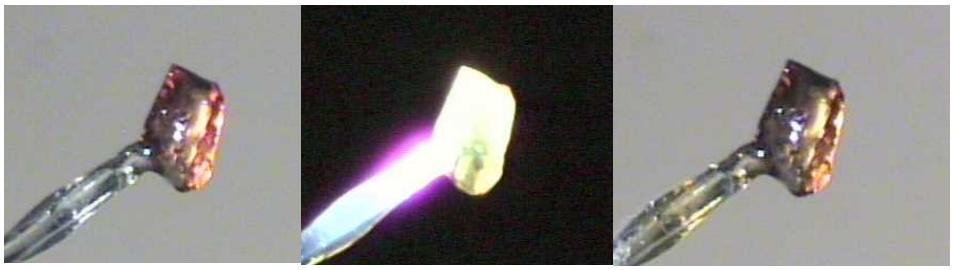


Figure S3. The crystal before (left),during (center) and after (right) laser exposure.

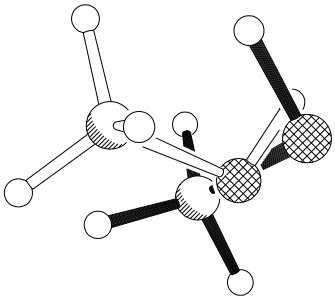


Figure S4. Shift in position and orientation of the methanol molecule on 3 hour exposure (solid bonds: molecule before exposure; open bonds: molecule after exposure).