Electronic Supplementary Information

Post-cycloaddition modification of a porous MOF for improved GC separation of ethanol and water

Ya-Jun Zhang,[a] Cheng Chen,[a] Li-Xuan Cai,[a] Bin Tan,[a] Xiao-Dong Yang,[b] Jie Zhang,[a,b] and Min Ji*[c]*

[*a*] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, The Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China, E-mail: zhangjie@fjirsm.ac.cn

[*b*] MOE Key Laboratory of Cluster Science, Beijing Key Laboratory of Photoelectronic/ Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing, 102488, P. R. China, E-mail: zhangjie68@bit.edu.cn

[*c*] School of Chemistry,Dalian University of Technology, Dalian 116024, Liaoning, P. R. China, E-mail: jimin@dlut.edu.cn

****

Additional Data

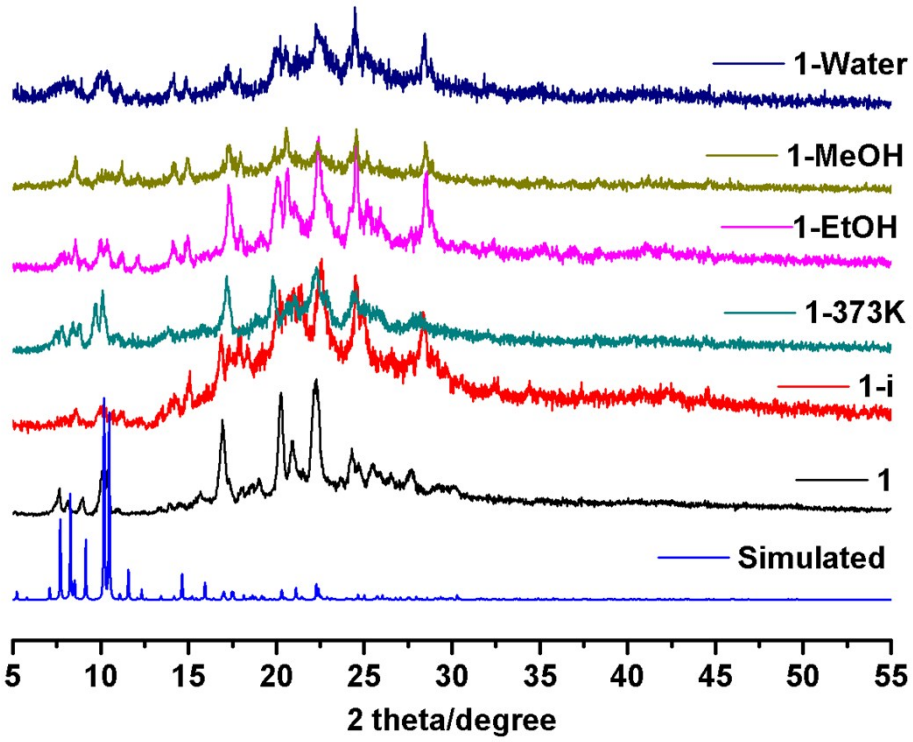


Fig.S1 (1) PXRD of simulated **1** based on the structure, crystal **1, 1-i** (irradiated under 365 nm UV light for 48 h)**, 1-373K** (heated at 373 K for 1h)**, 1-EtOH** (after adsorption-desorption test for EtOH vapor at 298 K)**, 1-MeOH** (after adsorption-desorption test for MeOH vapor at 298 K), **1-Water** (after adsorption-desorption test for Water vapor at 298 K).

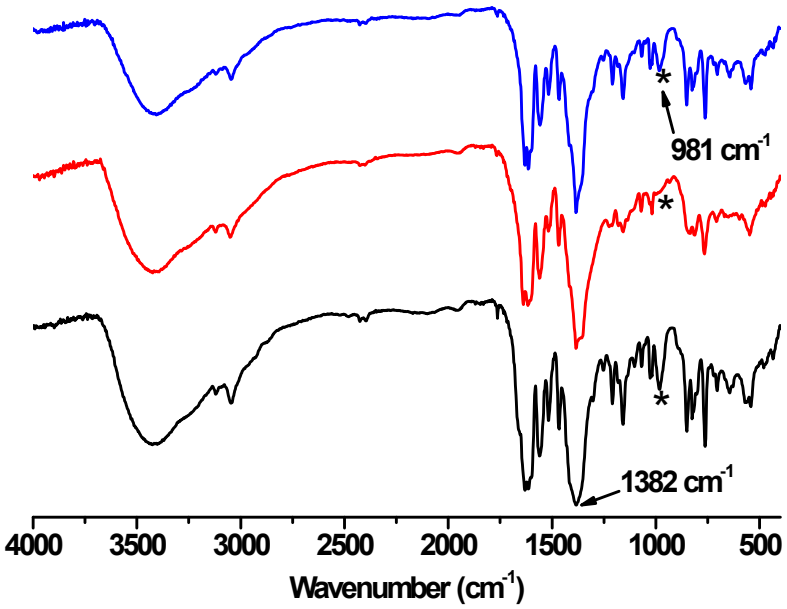


Fig. S2 In-situ FT-IR spectra of crystal **1** before (black) and after (red) irradiated by 365 nm UV light, the blue line is IR spectra of crystal **1** after heated at 373 K for one hour; The characteristic N-O vibration at 1382 cm^{-1} demonstrates that there is nitrate ion in the structure and the disappearance of the characteristic C–H vibration of trans RCH=CHR at 981 cm^{-1} after irradiated by 365 nm light demonstrates the occurrence of photoinduced structural transformation.

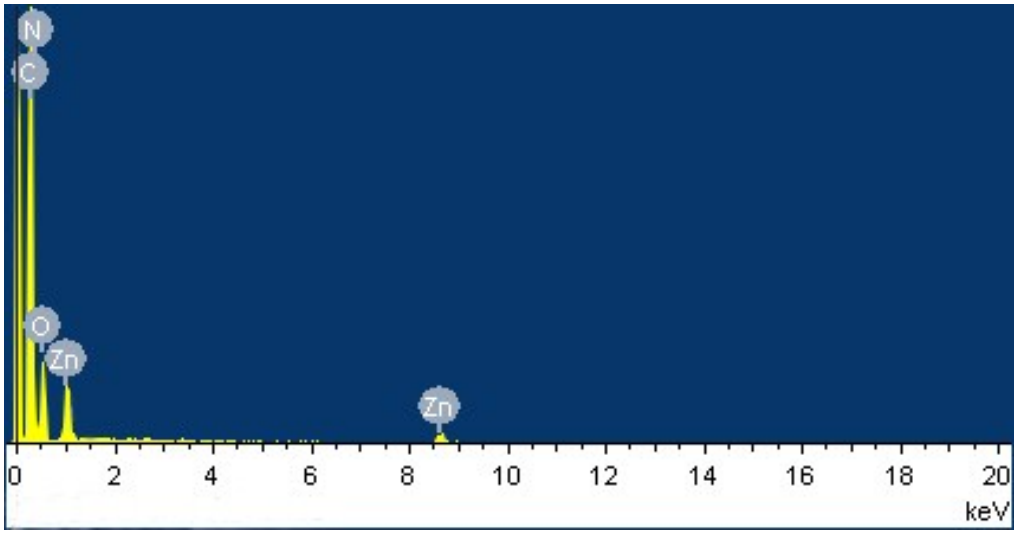


Fig.S3 Energy-dispersive X-ray spectroscopy (EDS) of **1** shows no Cl in the structure.

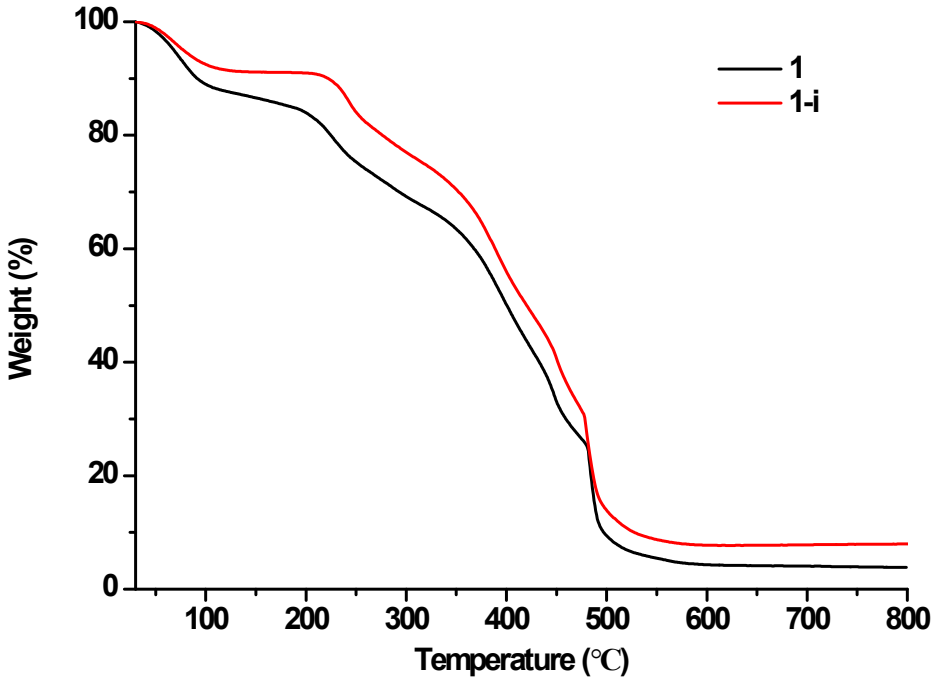


Fig. S**4** Thermogravimetric (TG) plots of compound **1**(black) and the photoirradiated sample **1-i** (red).

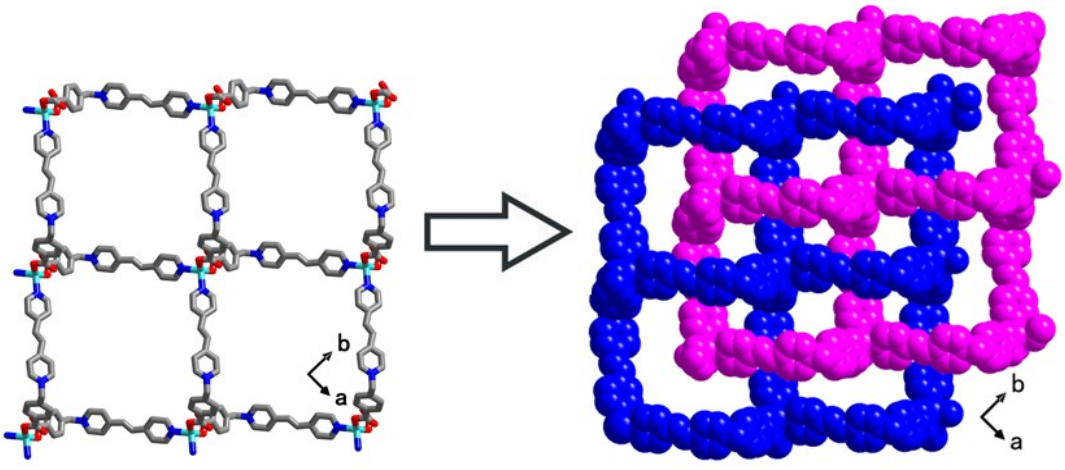
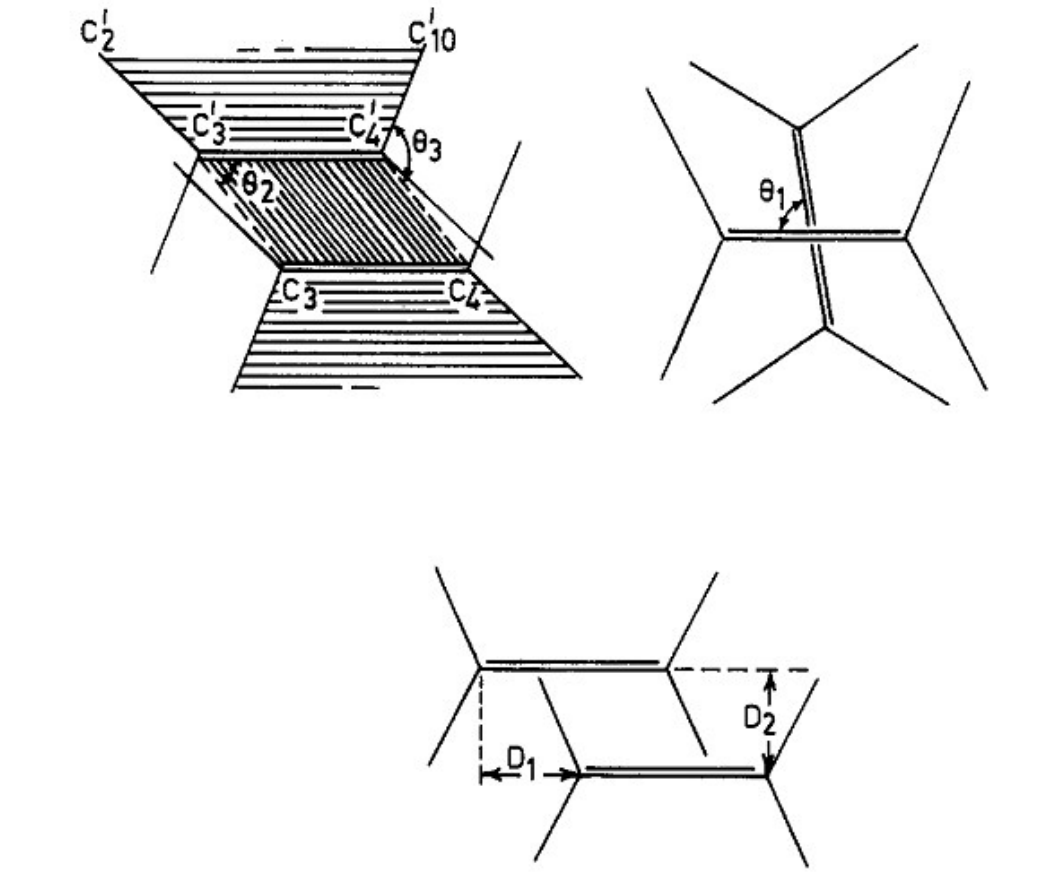


Fig.S5 Two independent networks interpenetrate each other in a 2D + 2D → 2D fashion, leading to a 2-fold interlocked bilayer.



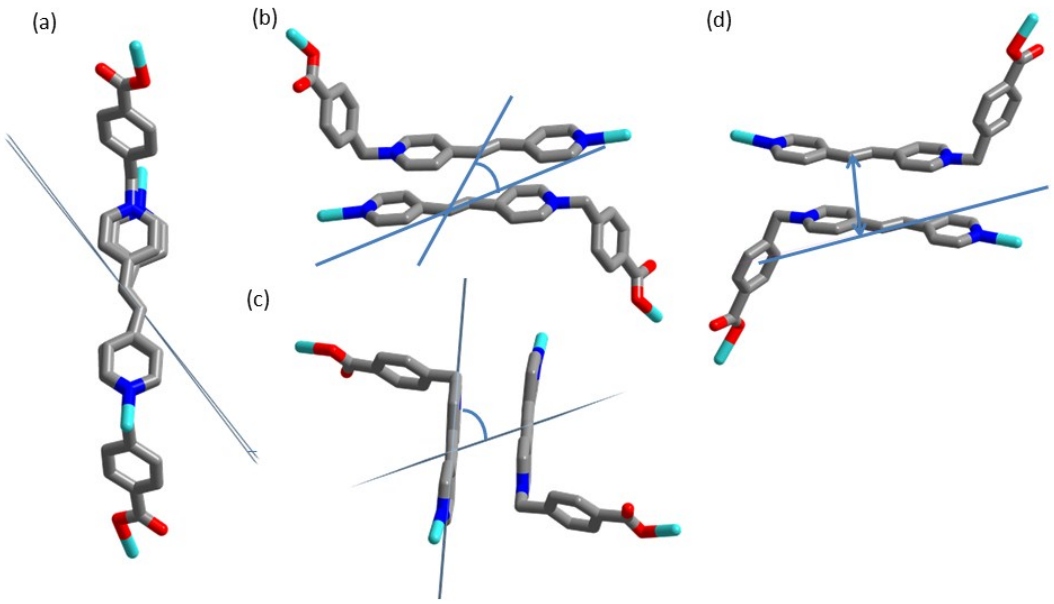


Fig.S6 Top: Schematic of definition of the parameters usually considered to be geometric criteria for [2+2] photodimerization of double bonds (According to Ref: V.Ramamurthy, K.Venkatesan, Chem. Rev. 1987, 87, 433–481; θ_3 is the angle between the >C=C< and C=C-C=C Planes). Bottom: The corresponding geometrical parameters θ_1(a), θ_2(b), θ_3(c) and D_2(d) in crystal **1** are 1.16°, 78.12°, 66.48° and 3.89 Å. D_1 is 0.82 Å gotten by calculation of $D_2/\tan\theta_2$.

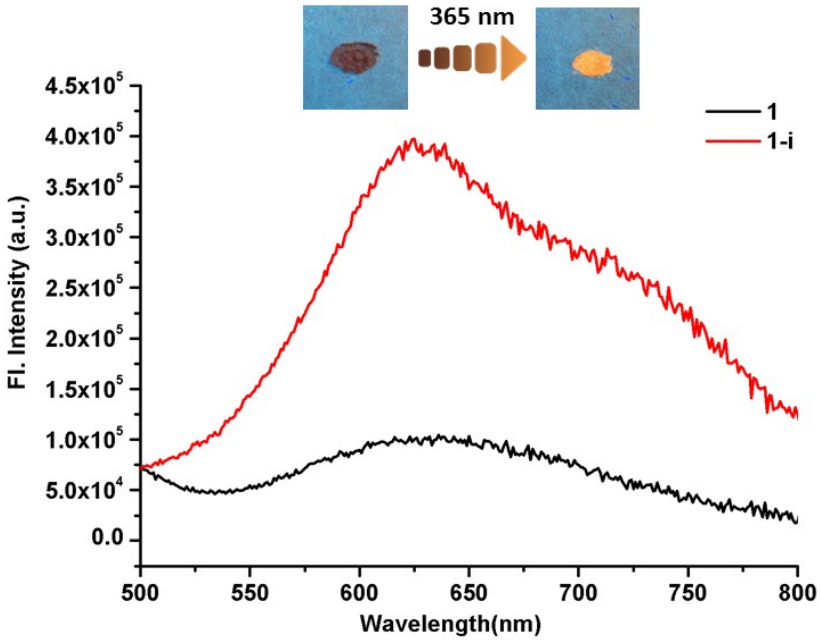


Fig. S7 Top panel: Fluorescence image of powdered crystal **1** upon UV irradiation. Bottom panel: The emission spectra of sample **1** before and after irradiated by 365 nm UV light, λ_{ex} = 330 nm.

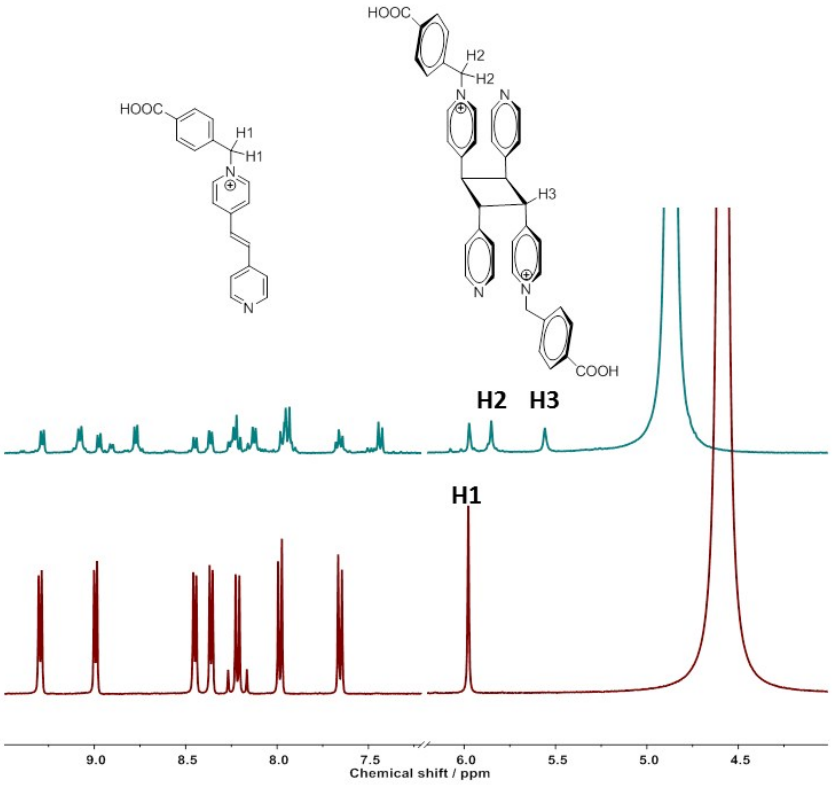


Fig. S8 ^{1}H NMR (400 MHz, DMSO-d_6) spectra showing the photocycloaddition of crystal **1** with a conversion yield of around 60% after the sample is subjected to 365nm UV radiation for 24 h (2 mW cm^{-2}).

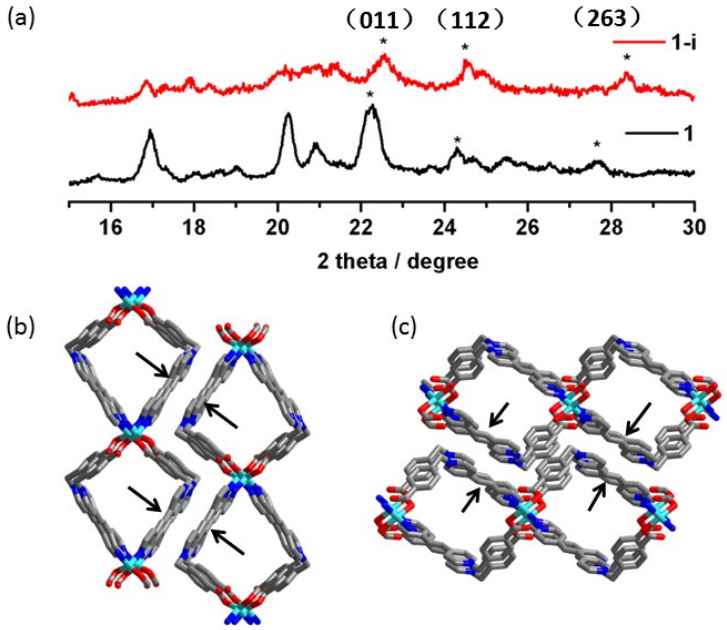


Fig.S9 (a)The PXRD patterns show the shifts of the (0 1 1), (1 1 2) and (2 6 3) peaks of crystal **1** after irradiated by 365nm UV light; (b) The corresponding PXRD peaks shift suggest the contraction of two adjacent layers due to the [2+2] cycloaddition reaction happened in crystal **1**.

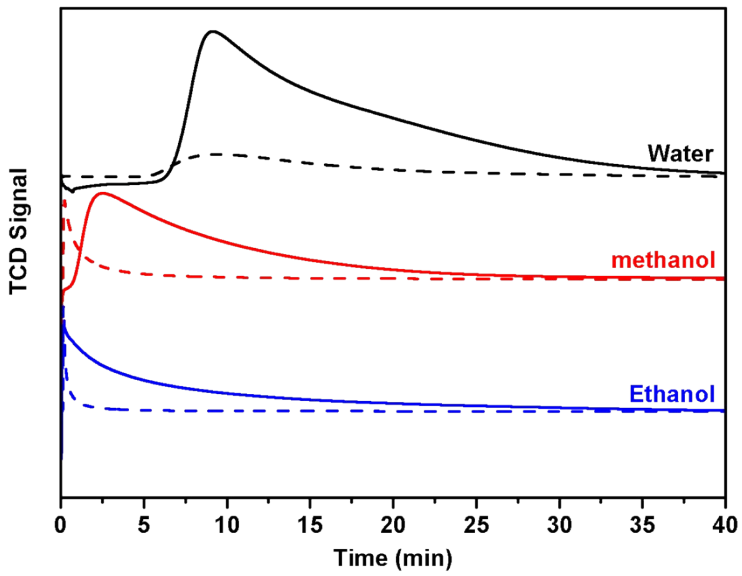


Fig. S10 The retention time of ethanol, methanol and water in the column filled with crystal **1** is 0.20 min, 2.51 min and 9.12 min respectively (solid line); The retention time of ethanol, methanol and water in the column filled with sample **1-i** is 0.16 min, 0.22 min and 9.07 min respectively (dash line).