

Supporting Information

Photoswitching storage of guest molecules in metal-organic framework for photoswitchable catalysis: exceptional product, ultrahigh photocontrol, and photomodulated size selectivity

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Experiments.

Materials and Physical Measurements. All the reagents used in this work are purchased from Alfa without any purification. Thermogravimetric analysis (TG) was performed by a TGA Q500 thermal analysis system under an air atmosphere from 40-800°C at a rate of 5°C /min. Data were analyzed using the TA Universal Analysis software package. X-ray powder diffraction were collected by a Bruker AXSD8 Discover powder diffractometer at 40 kV, 40 mA for Cu K α , ($\lambda = 1.5406\text{\AA}$). The simulated powder patterns were calculated by Mercury 1.4. The purity of the bulk products were determined by comparison of the simulated and experimental PXRD patterns. Infrared Spectra (IR) were measured by a Bruker VERTEX 70 spectrometer in the 500-4000 cm^{-1} region.

The gas sorption isotherms were collected on a Belsorp-max. Ultrahigh-purity-grade (>99.999%) N₂ and CO₂ gases were used in this adsorption measurement. To maintain the experimental temperatures liquid nitrogen (77 K) and temperature-programmed water bath (293 K) were used respectively.

Before carrying out adsorption experiments, the as-synthesized samples of **ECUT-50** (150 mg) were immersed in CH₃OH for three days, then degassed automatically in Belsorp-max at 60°C for 24 h to generate the activated samples of **ECUT-50a**. The photoswitching test for CO₂ adsorption is carried out under UV irradiation (365 nm) with the distance of more than 60 cm between samples and UV source to eliminate possible heating effect.

Synthesis of ECUT-50. A 10 mL DMF solution of InCl₃·6H₂O (1 mmol), H₂AzDC(2 mmol) was sealed in a Teflon reactor, and heated at 110°C for 3 days, and then cooled to room temperature at 3°C/h. Subsequently, red block crystals were obtained in 93% yield based on In. Elemental analysis is found to be C/49.65, H/9.46, N/19.38. Combination with the TG results that affords a major loss before 200°C (ca. 37%) suggests the chemical formula of [In(AzDC)₂][H₂N(CH₃)₂](DMF)_{5.5} for the as-synthesized samples (**ECUT-50**) after drying naturally, where the corresponding expected value is calculated to be C/49.29, H/9.65, N/19.16 and 36.5%.

X-ray Crystallography. X-ray diffraction data of **ECUT-50** and the products were collected respectively at 110K and room temperature on a Bruker-AXS SMART Breeze CCD diffractometer using graphite monochromated MoK α radiation ($\lambda=0.71073\text{\AA}$). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on

their respective atoms. The SQUEEZE subroutine of the PLATON software²⁷ suite was used to remove the scattering from the highly disordered guest molecules. CCDC 1510477-1510485 contains the supplementary crystallographic data of ECUT-50 and the products. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT calculations. The structural optimization was performed with DMol ab initio quantum chemistry software of Accelrys' materials studio. The calculations were performed with the 6-31G basis sets, double numerical basis sets supplemented by polarization functions. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof exchange-correlation function was adopted. SCF density convergence, optimization energy convergence and gradient convergence equal to 0.00001, 0.0001 and 0.02 a.u, respectively.

The calculations of benzaldehyde-loaded configuration were carried out using the Gaussian 09 program package.

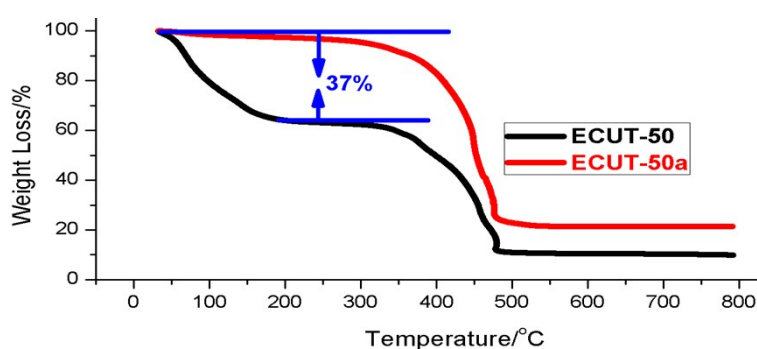


Fig. S1 The TG plots of ECUT-50 and ECUT-50a.

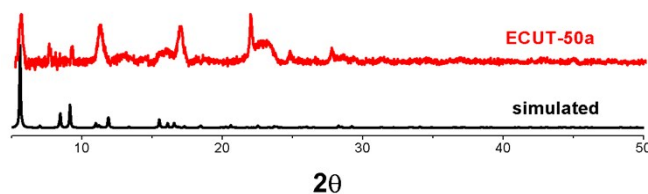


Fig. S2 The PXRD patterns simulated from the crystal data of ECUT-50, of the activated samples (ECUT-50a).

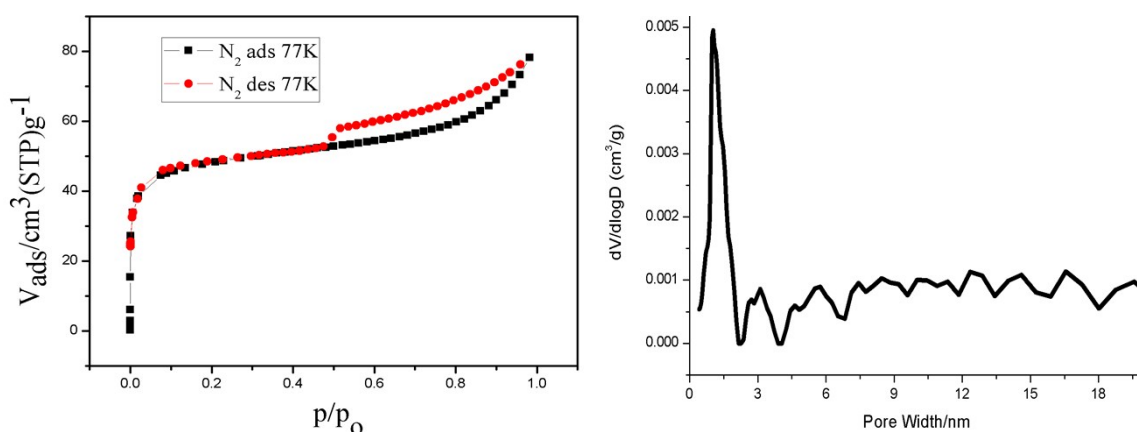


Fig. S3 The N₂ adsorption at 77K and its corresponding pore size distributions (PSDs) calculated by NLDFT.

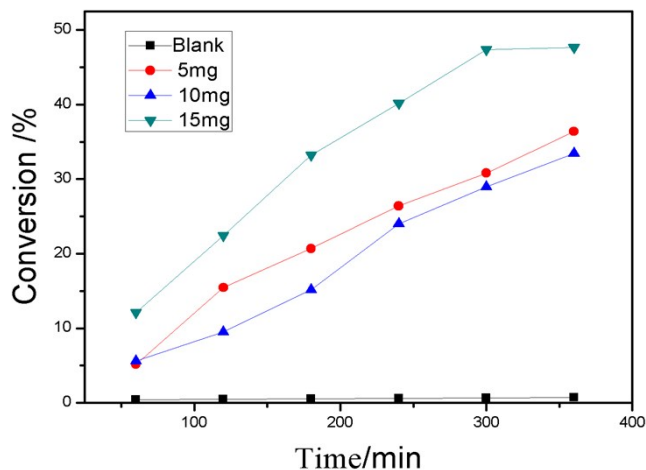


Fig. S4 The effect of dosage of catalyst on the conversion of benzaldehyde. Reactions were performed with 1mmol benzaldehyde and 1mmol cyanoethylacetate in 10 mL C₂H₅OH with set amount of catalyst of ECUT-50a for 6 h at 55° C.

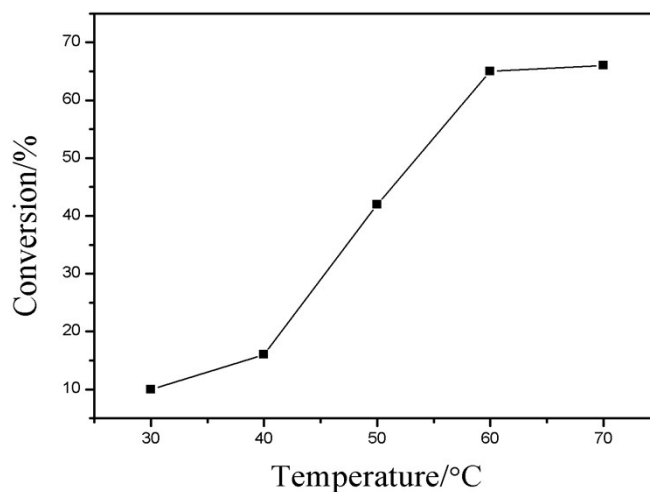


Fig. S5 The effect of reaction temperature on the conversion of benzaldehyde. Reactions were performed with 1mmol benzaldehyde and 1mmol cyanoethylacetate in 10 mL C₂H₅OH with 15 mg catalyst of ECUT-50a for 6 h at set temperature.

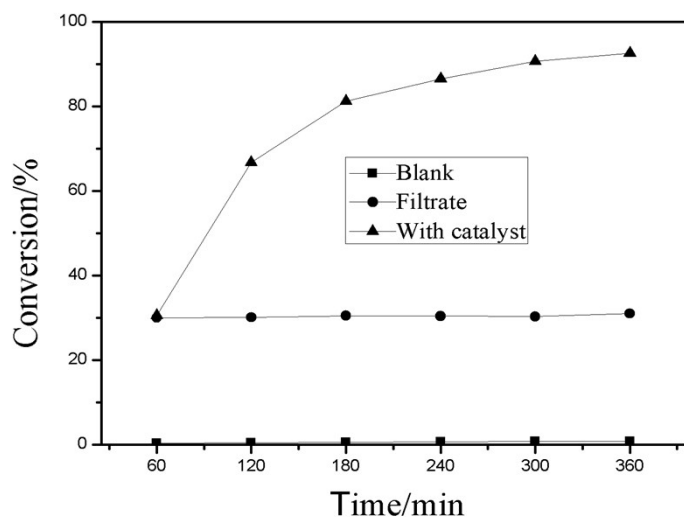


Fig. S6 The catalysis reaction with the catalyst of ECUT-50a filtrated from the reaction solution. Reactions were

performed with 1mmol 2-nitrobenzaldehyde and 1mmol cyanoethylacetate in 10 mL C₂H₅OH with 15 mg catalyst or without catalyst for 6 h at 60°C.

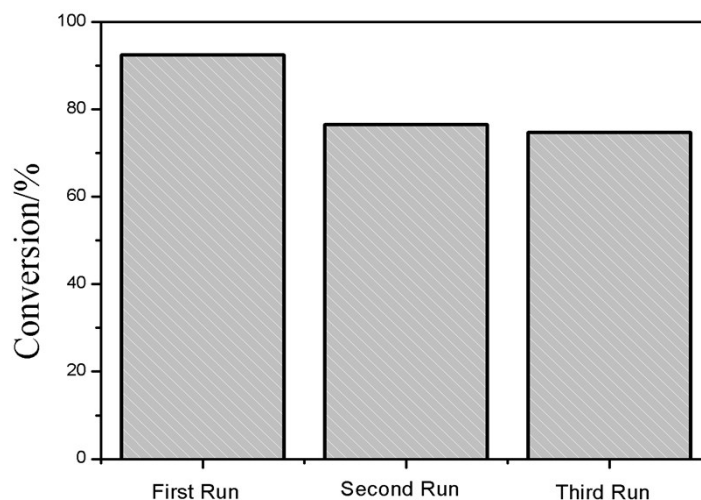


Fig. S7 The recycle of **ECUT-50a** to catalyze the Knoevenagel condensation reaction between 2-nitrobenzaldehyde and cyanoethylacetate. Reactions were performed with 1mmol 2-nitrobenzaldehyde and 1mmol cyanoethylacetate in 10 mL C₂H₅OH with 15 mg catalyst or without catalyst for 6 h at 60°C.

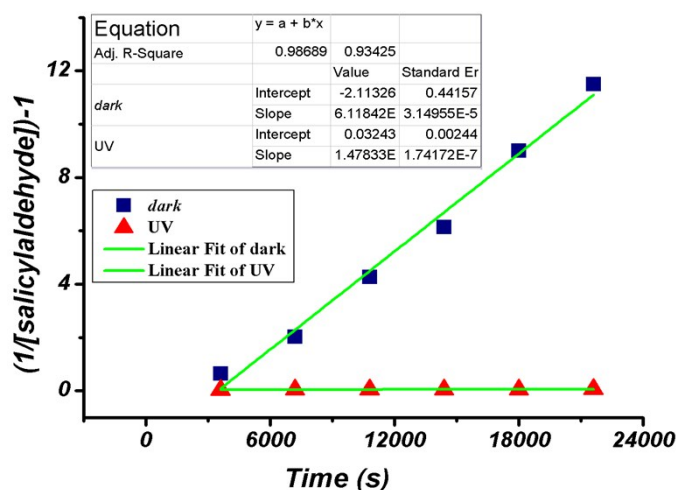


Fig. S8 Plot of $(1/[\text{salicylaldehyde}])^{-1}$ (mmol) vs. time (s) for the Knoevenagel condensation and Michael addition reaction between salicylaldehyde and cyanoethylacetate catalyzed by **ECUT-50a**. Two reactions were run concurrently with one exposed to UV (365 nm) for 6 h and one kept in the dark.

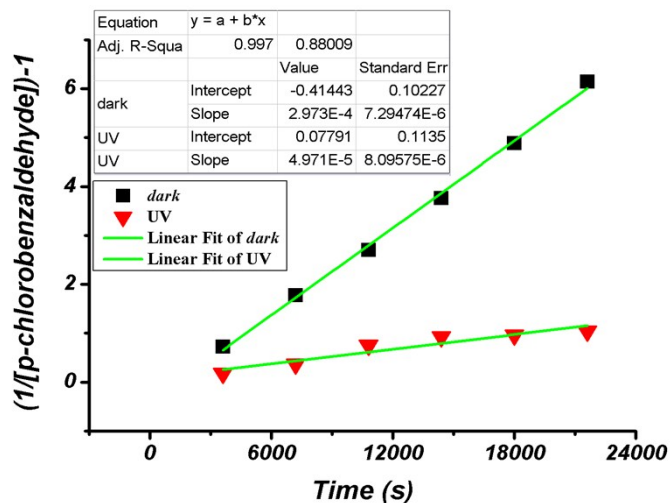


Fig. S9 Plot of $(1/[p\text{-chlorobenzaldehyde}])^{-1}$ (mmol) vs. time (s) for the Knoevenagel condensation and Michael addition reaction between 2-chlorobenzaldehyde and cyanoethylacetate catalyzed by **ECUT-50a**. Two reactions were run concurrently with one exposed to UV (365 nm) for 6 h and one kept in the dark.

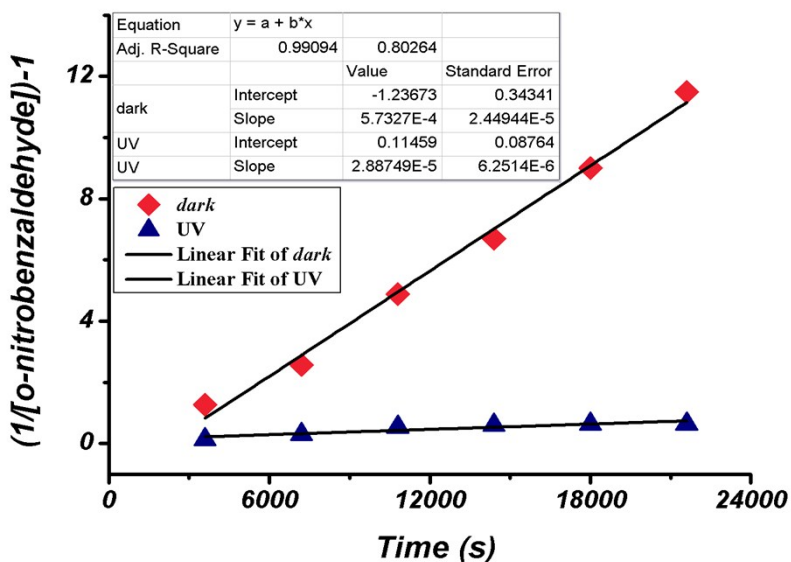


Fig. S10 Plot of $(1/[o\text{-nitrobenzaldehyde}])^{-1}$ (mmol) vs. time (s) for the Knoevenagel condensation and Michael addition reaction between 2-nitrobenzaldehyde and cyanoethylacetate catalyzed by **ECUT-50a**. Two reactions were run concurrently with one exposed to UV (365 nm) for 6 h and one kept in the dark.

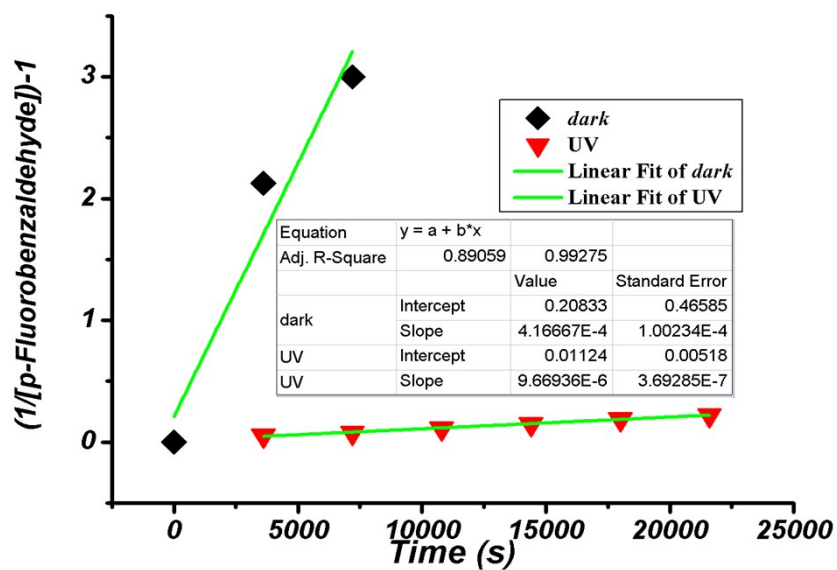


Fig. S11 Plot of $(1/[4\text{-fluorobenzaldehyde}])^{-1}$ (mmol) vs. time (s) for the Knoevenagel condensation and Michael addition reaction between 4-fluorobenzaldehyde and cyanoethylacetate catalyzed by **ECUT-50a**. Two reactions were run concurrently with one exposed to UV (365 nm) for 6 h and one kept in the dark.

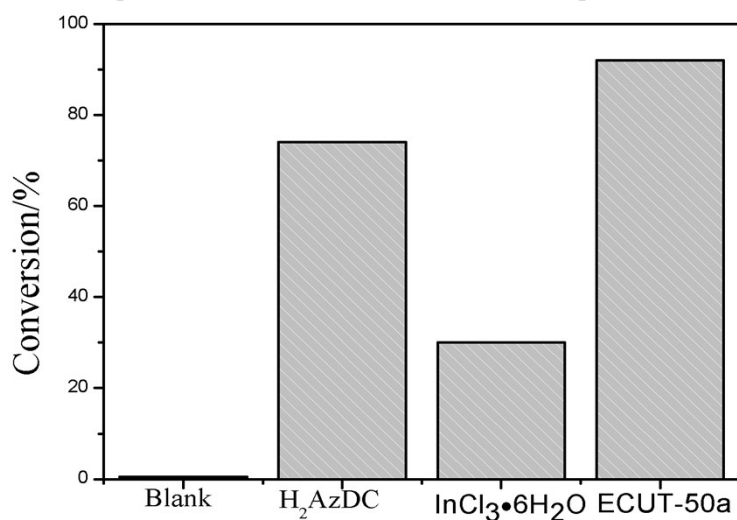


Fig. S12 The catalysis test for these sources such as H₂AzDC, InCl₃, and **ECUT-50a**. Reactions were performed with 1mmol 2-nitrobenzaldehyde and 1mmol cyanoethylacetate in 10 mL C₂H₅OH with 15 mg catalyst or without catalyst for 6 h at 60°C.

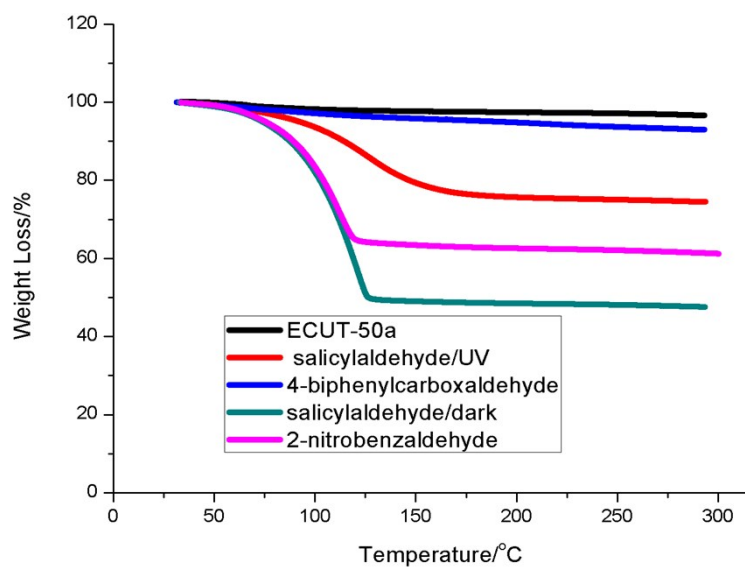


Fig. S13 The TG plots of the **ECUT-50a** samples and the samples after loading of selected aldehyde substrates.

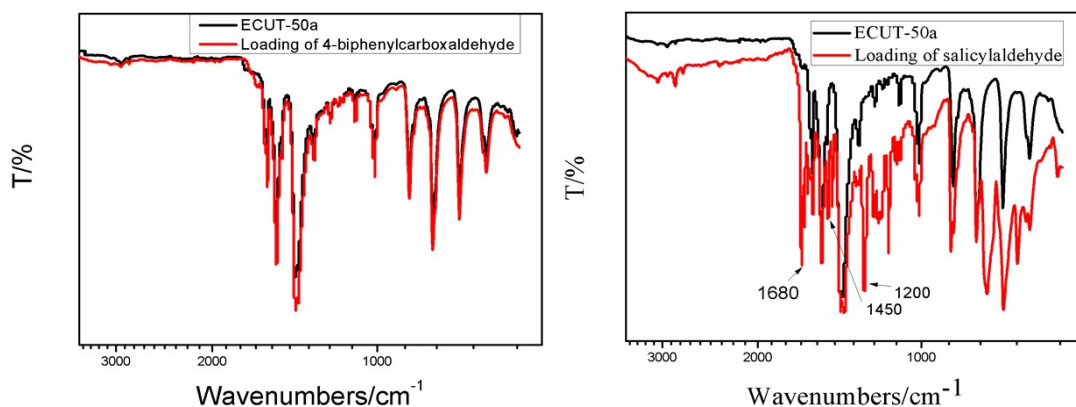


Fig. S14 The IR bonds of **ECUT-50a** and the samples after loading of selected aldehyde substrates. It is clear that 4-biphenylcarboxaldehyde could not be loaded and salicylaldehyde is loaded.

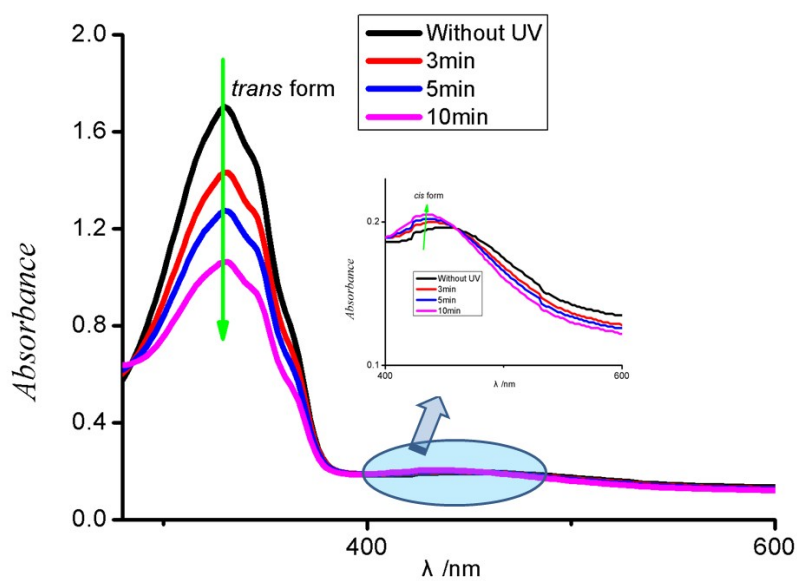


Fig. 15 The UV-Vis spectrum of **ECUT-50a** in the dark or UV (365nm).

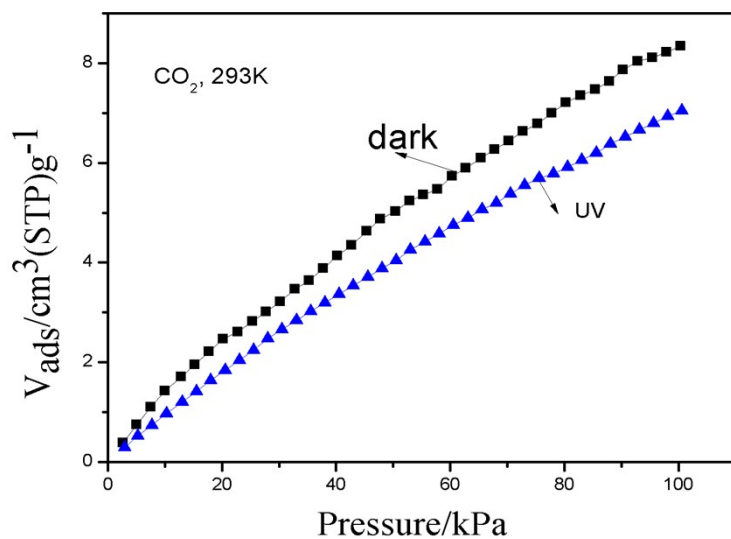


Fig. S16 The CO₂ adsorption of ECUT-50a in the dark or UV (365nm).

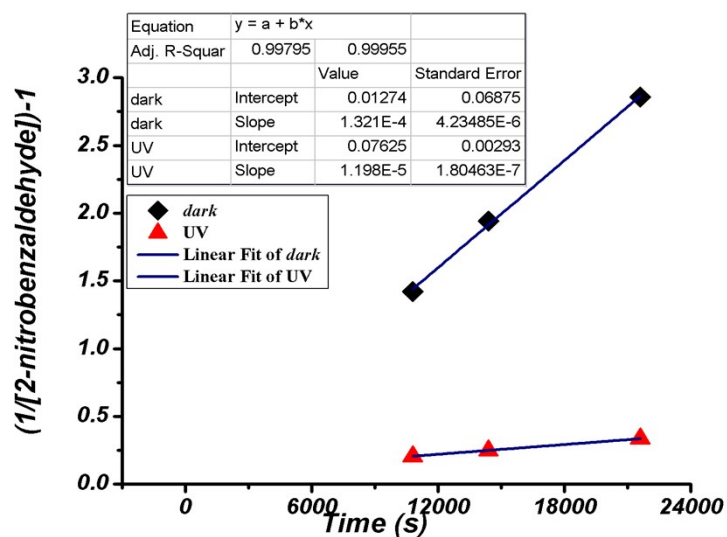
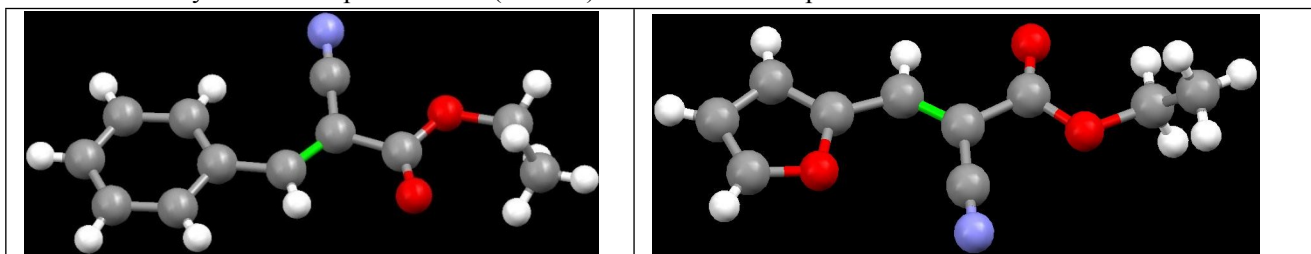


Fig. S17 Plot of $(1/[2\text{-nitrobenzaldehyde}])^{-1}$ (mmol) vs. time (s) for the Knoevenagel condensation and Michael addition reaction between 2-nitrobenzaldehyde and cyanoethylacetate catalyzed by H₂AzDC. Two reactions were run concurrently with one exposed to UV (365 nm) for 6 h and one kept in the dark.



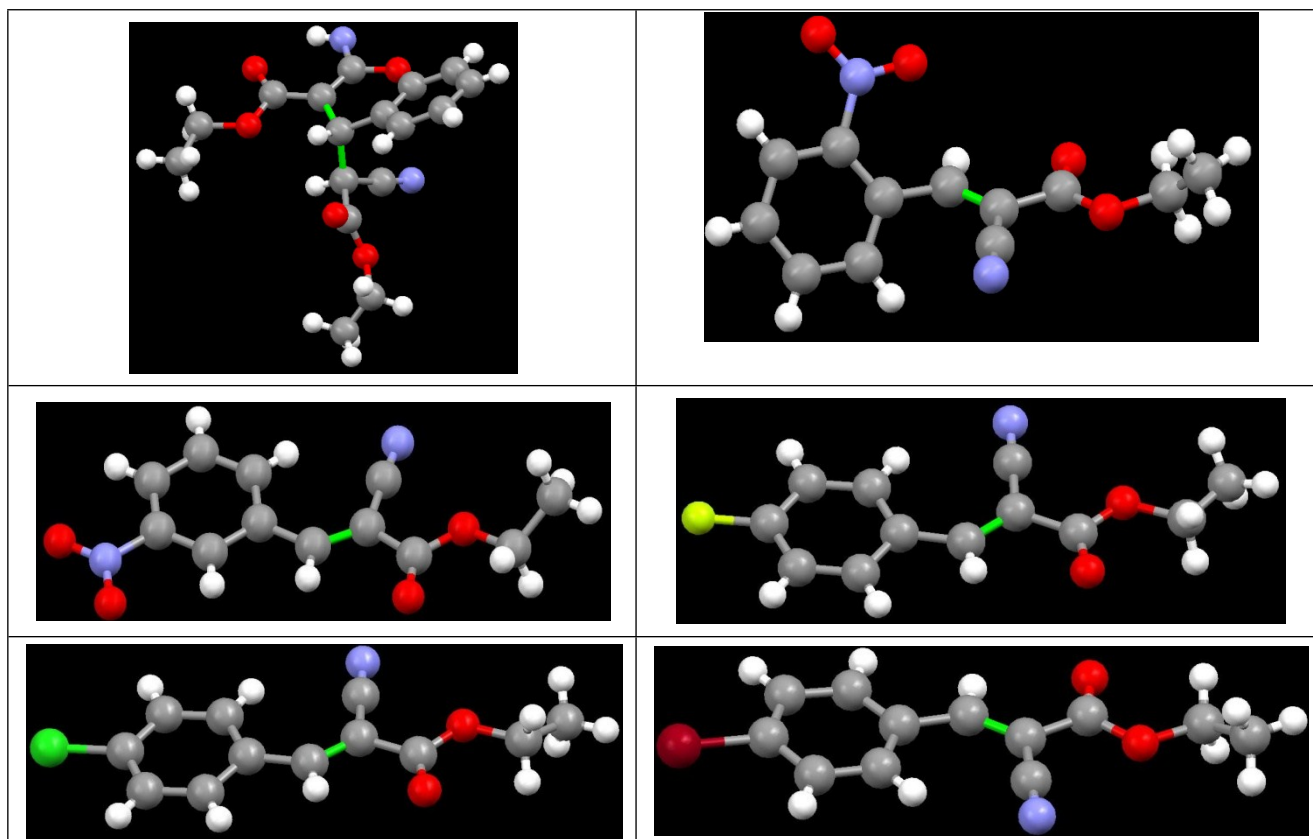


Fig. S18 The crystal structure of these products. The green bonds are the new formed carbon-carbon bond.