Supplementary Information

A Reversible Photochromic Covalent Organic Framework

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Supplementary Sections

Synthesis of DBTB

4, 4'-dihydroxy-[1, 1'-biphenyl]-3, 3', 5, 5'-tetracarbaldehyde (DBTB) was synthesized according to the published procedure (*Dyes and Pigments*, 2022, 203, art. no. 110342). HMTA (hexamethylenetetramine, 107.40 mmol, 15.06 g) was added into a dried round-bottom flask. The flask was purged with argon, and TFA (trifluoroacetic acid, 100 mL) was added. After completely dissolving HMTA, biphenyl-4,4′-diol (10.740 mmol, 2.00 g) was rapidly added. After confirming that the mixture turned to an orange color, the mixture was heated at $120\,^{\circ}$C for 7 days. The product was dark red, and it was poured into 4N HCl (200 mL) to isolate the yellow precipitate. The precipitate was recrystallized with hot DMSO to obtain 4.92 g of yellow microcrystals (yield: 58%). ^{1}H NMR (400 MHz, DMSO-d$_6$). δ (ppm): 11.68 (s, 2H), 10.34-10.33 (d, 4H), 8.43-8.42 (d, 4H). ^{13}C NMR (100 MHz, DMSO-d$_6$). δ (ppm): 124.57, 135.05, 161.92, 193.09.

Synthesis of DETH

2, 5-diethoxyterephthalohydrazide (DETH) was synthesized according to the published procedure (*J. Am. Chem. Soc.* 2020, 142, 12146). Diethyl-2,5-dihydroxyterephthalate (4 mmol, 1.05 g) and potassium carbonate (13.2 mmol, 1.82 g) were suspended in acetonitrile (10 mL). Iodoethane (13.2 mmol, 1.07 mL) was added. After the reaction mixture was refluxed for 72 h, the solvent was removed. The brownish residue was added into water and extracted with ethyl acetate. The organic extract was dried over magnesium sulfate. The solvent was removed to give the product as a light yellow solid, the yield is about 97%, no further purification is required, and it is directly applied to the next step of synthesis. Then the yellow solid product (3.96 mmol, 1.20 g) was suspended in a solution of ethanol/toluene (20 mL, 1:1). Hydrazine hydrate (39.6 mmol, 1.94 mL) was added. The reaction mixture was heated to 110 ℃ for 8 h. The solvent was evaporated to yield an off-white solid (903 mg, 3.20 mmol, 81%). ^{1}H-NMR (400 MHz, DMSO-d$_6$): δ = 9.24 (s, 2H), 7.38 (s, 2H), 4.58 (s, 4H), 4.12 (q, 4H), 1.35 (t, 6H) ppm. ^{13}C-NMR (100 MHz, DMSO-d$_6$): δ = 163.8, 149.53, 125.0, 114.7, 64.81, 14.54 ppm.

Synthesis of N'-(2-Hydroxybenzylidene)benzohydrazide

Benzoyl hydrazine (1.0 mmol, 136 mg), Salicylaldehyde (1.0 mmol, 122 mg) and acetic acid (6M, 1.0mL) was dissolved in CH$_3$OH (30 mL), and the solution was refluxed for 3 h. After cooling to room temperature, the resulting precipitate was collected by filtration, washed with CH$_3$OH, and dried under vacuum to get light yellow crystal (Supplementary Figure 7). Yield: 85%.

Synthesis of N',N'',N''',N''''-((1E,1'E,1''E,1'''E)-(4,4'-dihydroxy-[1,1'- biphenyl]-3,3',5,5'-tetrayl) tetrakis (methanylidene)) tetra (benzohydrazide)

30 mL of ethanol was added into a reactor containing DBTB (1.678 mmol, 0.50 g). While stirring the mixture, benzoyl hydrazine (6.712 mmol, 0.92 g,) was added. The reactor was sealed and heated at 100 ℃ for 8 hours. The reaction mixture was cooled to room temperature, and then poured into 100 mL of water. The resulting precipitate was isolated by filtration, and washed with acetone to obtain a product in the form of a yellow powder. Yield: 75% (Supplementary Figure 8). ^{1}H NMR (400 MHz, DMSO-d$_6$). δ (ppm): 12.75 (s, 2H), 12.29 (s, 4H), 8.89 (s, 4H), 8.18-7.93 (m, 12H), 7.60 (dt, J = 27.5, 7.4 Hz, 12H). ^{13}C NMR (100 MHz, DMSO-d$_6$). δ (ppm): 163.56, 156.62, 146.51, 133.37, 132.49, 131.11, 130.11, 129.03, 128.20, 121.22. ESI-MS: calcd for C$_{44}$H$_{34}$N$_8$O$_6$, 769.2504 ([M-H$^+$]), found: m/z 769.2443.

Synthesis of DBTB-DETH-COF under ultrasound conditions at 0 ℃

The DBTB-DETH-COF prepared by ultrasound with the monomers of DBTB (135 mmol, 3.55 g)

and DETH (265 mmol, 7.50 g) in the dioxane/mesitylene (200.0 / 200.0 mL). After stirring for 2 min, acetic acid (6M, 50.0mL) was added, and the above solution was kept under ultrasound conditions (200 W, 80 kHz) at 0 ℃ for 1 h. After that, the resultant yellow precipitate denoted as DBTB-DETH-COF was filtered and washed with DMF, dichloromethane and ethanol, and finally dried in vacuum at 80 ℃ overnight (94 % yield).

Synthesis of DBTB-DTPH-COF under solvothermal conditions

A mixture of DBTB (0.135 mmol, 35.25 mg), DETH (0.265 mmol, 75 mg) and acetic acid (6M, 1.0mL) in the dioxane/mesitylene (5.0/5.0 mL) mixture was sealed in a Pyrex tube (35 mL) and heated under N_2 at 120 ℃ for 3 days. The solids were then separated via centrifugation after it was to room temperature. The generated yellow powder was completely washed with DMF, dichloromethane and ethanol and dried in vacuum to white produce DBTB-DTPH-COF in 92 % yield.

Chemical stability test of DBTB-DTPH-COF

The sample of DBTB-DTPH-COF (3 mg) was stored under static conditions for the predetermined amount of time in 0.5 mL HCl (6 M) at room temperature for 3 days, NaOH (1 M) in H_2O solution at room temperature for 3 days, $NaBH_4$ (1 M) in methanol at room temperature for 3 days and 0.5 mL trifluoroacetic acid (TFA) at room temperature for 3 days, The sample was washed with ethyl alcohol for 3 times, dried under vacuum at 60 ℃ and measured by PXRD measurements and FT-IR spectra.

Instruments

The powder diffractometer (XRD) patterns were collected by a D8 ADVANCEX-ray with Cu Kα radiation (λ = 1.5405 Å). UV-vis diffuse reflectance spectra (DRS) and ultraviolet-visible absorption spectrum were performed on Shimadzu UV-3600, the test range was from 200 to 800 nm. The total surface areas of the DBTB-DETH-COF were measured by the BET (Brunauer–Emmer–Teller) method using N_2 adsorption at 77 K, this was done by the Micromeritics ASAP 2000 sorption/desorption analyzer. Infrared (IR) sample was prepared as KBr pellets, and spectra were obtained in the 400-4000cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Bruker Avance NMR spectrometer (400 MHz). ^{13}C NMR spectra were recorded on a MERCURY plus 400 spectrometer operating at resonance frequencies of 400 MHz. Thermogravimetric analyses (TGA) were carried out under flowing nitrogen at a heating rate of 10 ℃·min^{-1} on a TA Instrument Q5 analyzer. XPS spectra were obtained from PHI Versaprobe II. TEM (transmission electron microscopy) analysis was performed on a JEOL 2100 Electron Microscope at an operating voltage of 200 kV. Scanning electron microscopy (SEM) images were taken on a SUB010 scanning electron microscope with acceleration voltage of 20 kV. Electron paramagnetic resonance (EPR) signals were recorded on a Bruker A500 spectrometer at room temperature under visible-light irradiation using a Xe lamp (300W with the intensities 2.5W cm^{-2}). The transient absorption measurements were performed using a fiber laser (1030 nm, 100kHz repetition rate, 9.5 μJ/pulse, YF-FL-10-100-IR, Yacto-Technology, China) as the laser source and a femto-TA100 spectrometer (Time-Tech Spectra, China).

Simulated structure of DBTB-DETH-COF

Structural modeling of DBTB-DETH-COF was generated using the Materials Studio (ver. 2018) suite of programs. Molecular geometry optimization was performed with MS DMol3 module. The initial lattice was created by starting with the space group *P*1. The *a* and *b* lattice parameters

(initially 20.6000 Å) were estimated according to the center to center distance between the vertices of the COF. The constructed model was geometry optimized using the Forcite module (Universal force fields, Ewald summations). Then the calculated PXRD pattern was generated with the Reflex Plus module. Finally, Pawley refinement was applied for profile fitting, producing the refined PXRD profile with the lattice parameters of $a = b = 20.4000 (\pm 0.002)$ Å and $c = 3.4200 (\pm 0.002)$ Å. Rwp and Rp values converged to 2.09 % and 1.56%, respectively. Reflex Module in Material Studio using data from $2\theta = 2.0\text{-}30°$. Backgrounds were first refined applying a 2nd order Chebyschev Polynomial.

Supplementary Table 1. Crystal data and structure refinement for N'-(2-Hydroxybenzylidene)benzohydrazide

| Empirical formula	$C_{14}H_{12}N_2O_2$
Formula weight	240.26
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system, space group	Orthorhombic, Pna2
Unit cell dimensions	$a = 20.9124(19)$ Å $\alpha = 90$ deg.
	$b = 5.0405(3)$ Å $\beta = 90$ deg.
	$c = 10.7996(7)$ Å $\gamma = 90$ deg.
Volume	1138.37(14) Å^3
Z, Calculated density	1, 1.381 Mg/m^3
Absorption coefficient	1.097 mm-1
F(000)	484
Crystal size	0.21 x 0.04 x 0.03 mm
Theta range for data collection	4.228 to 70.254 °
Index ranges	-25<=h<=24, -3<=k<=6, -6<=l<=13
Reflections collected / unique	2710 / 1419 [R(int) = 0.0536]
Completeness to theta = 67.679	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1419 / 1 / 211
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0587, wR2 = 0.1600
R indices (all data)	R1 = 0.0633, wR2 = 0.1657
Largest diff. peak and hole	0.241 and -0.376 e.Å^{-3}

Supplementary Table 2. Selected bonds lengths and angles for N'-(2-Hydroxybenzylidene)benzohydrazide

|			
C(8)-O(2)	1.229(6)	C(8)-N(2)	1.358(6)
C(8)-C(9)	1.500(6)	O(1)-C(3)	1.358(6)
N(1)-C(1)	1.279(6)	N(1)-N(2)	1.373(5)
O(2)-C(8)-N(2)	122.4(4)	O(2)-C(8)-C(9)	121.0(4)
N(2)-C(8)-C(9)	116.5(4)	C(1)-N(1)-N(2)	117.6(4)

N(1)-C(1)-C(2)	121.0(4)
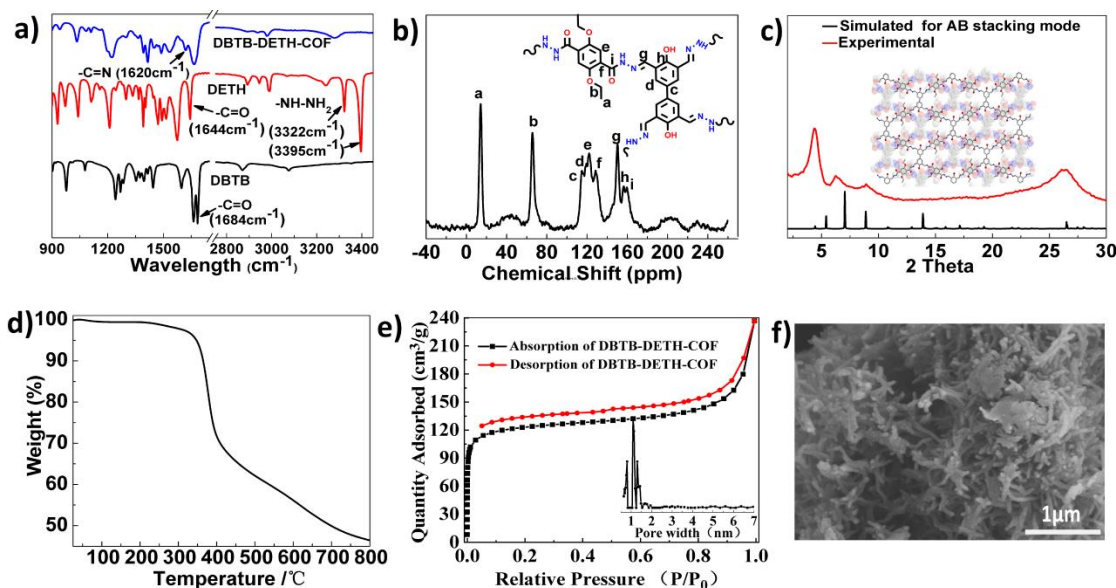
Supplementary Figure 1. The characterization of DBTB-DETH-COF. **a)** FT-IR spectra of DBTB, DETH and DBTB-DETH-COF. **b)** The solid state ^{13}C cross-polarization magic-angle-spinning (CP-MAS) NMR of DBTB-DETH-COF. **c)** The comparison between the experimental and simulated patterns for eclipsed (AB) stacking mode. **d)** TGA of DBTB-DETH-COF. **e)** BET of DBTB-DETH-COF at 77 K. The inset shows the pore-size distribution. **f)** SEM images of DBTB-DETH-COF.
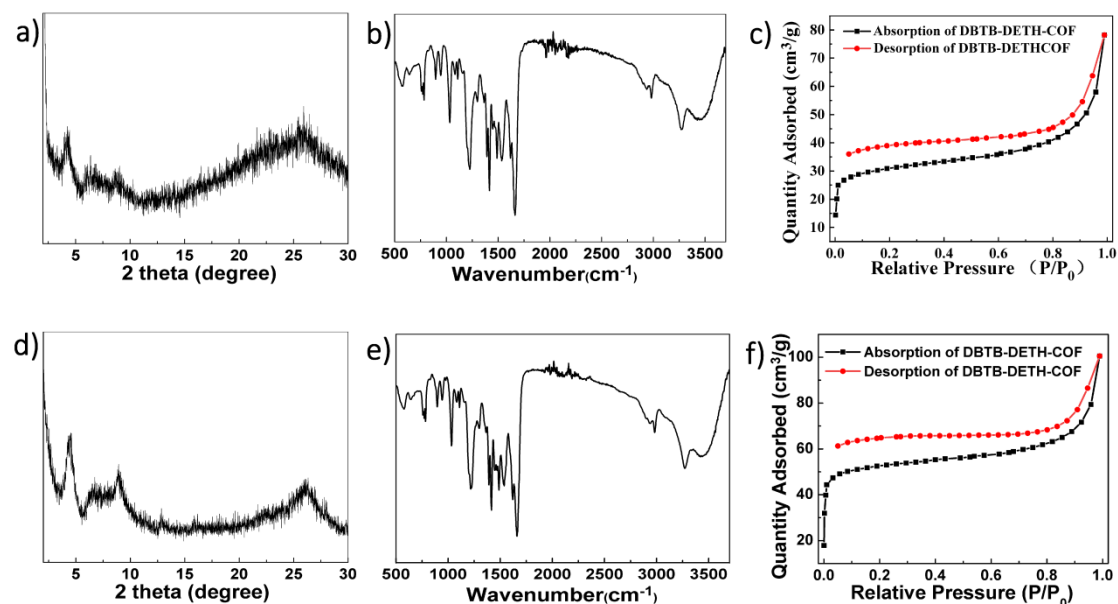

Supplementary Figure 2. The characterization of DBTB-DETH-COF under ultrasound at 0 ℃ for 1 hour and heating at 60 ℃ for 1 hour. **a)** the PXRD, **b)** FT-IR spectra, and **c)** BET of DBTB-DETH-COF synthesized under heating at 60 ℃ for 1 hour, and **d)** the PXRD, **e)** FT-IR spectra, **f)** BET of DBTB-DETH-COF synthesized under ultrasound condition at 0 ℃ for 1 hour.
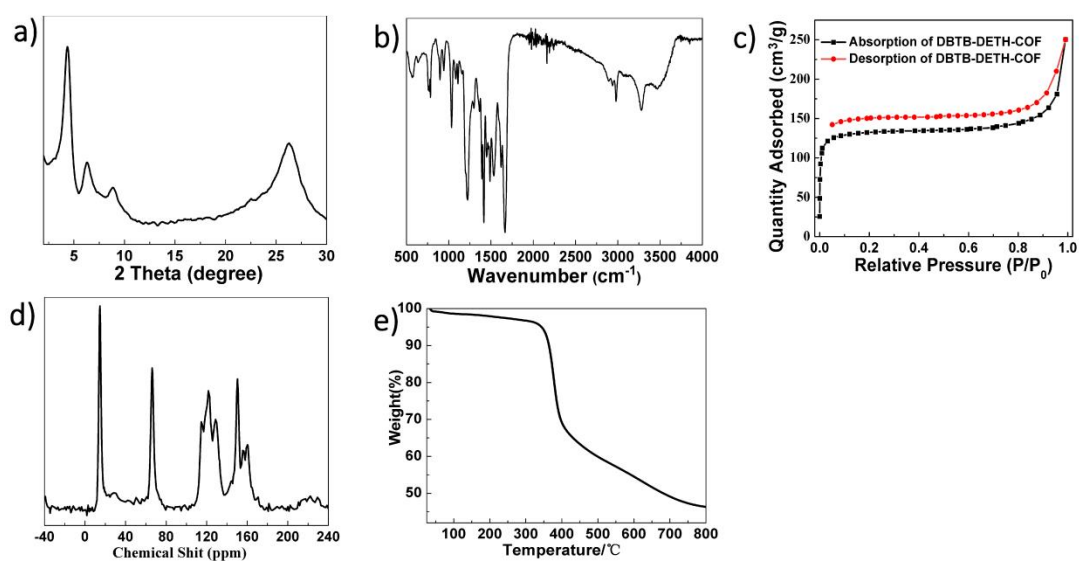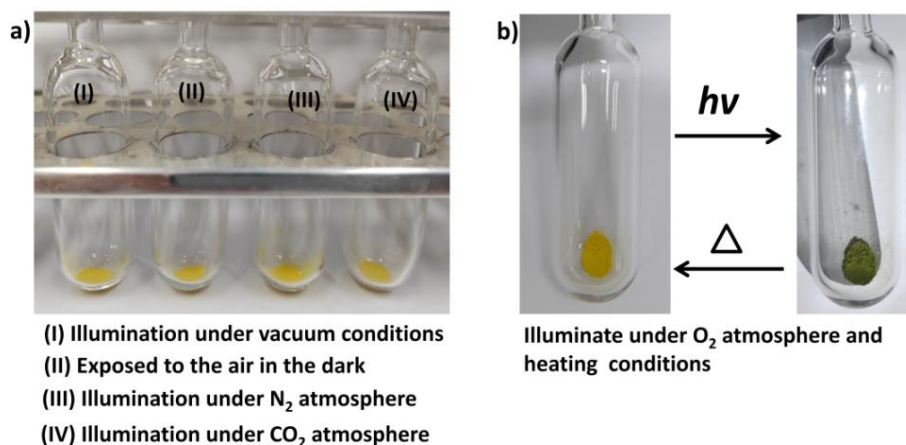
Supplementary Figure 3. The characterization of DBTB-DETH-COF synthesized under solvothermal conditions. **a)** the PXRD, **b)** FT-IR and **c)** BET, **d)** The solid state ^{13}C cross-polarization magic-angle-spinning (CP-MAS) NMR, **e)** TGA of DBTB-DTPH-COF.
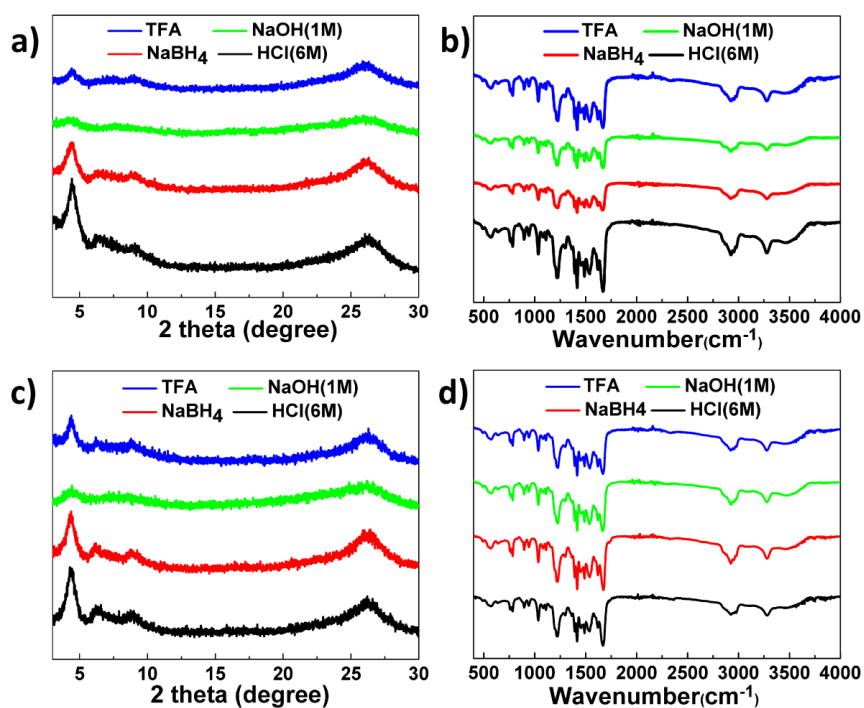

Supplementary Figure 4. The stability of DBTB-DTPH-COF formed through solvothermal method and the ultrasound method. **a)** the PXRD and **b)** FT-IR of DBTB-DTPH-COF synthesized under ultrasound condition in different media 3d at RT. **c)** the PXRD patterns and **d)** FT-IR of DBTB-DTPH-COF synthesized under solvothermal conditions in different media 3d at RT.
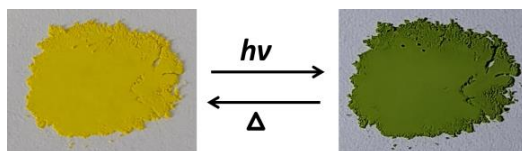
Supplementary Figure 5. The photochromism of DBTB-DTPH-COF synthesized under solvothermal conditions.

(I) Illumination under vacuum conditions
(II) Exposed to the air in the dark
(III) Illumination under N_2 atmosphere
(IV) Illumination under CO_2 atmosphere

Illuminate under O_2 atmosphere and heating conditions

Supplementary Figure 6. The photochromic features of DBTB-DETH-COF under different conditions. **a**) No photochromic phenomenon under vacuum, dark, nitrogen or carbon dioxide atmosphere when illuminated. **b**) photochromism occurs under oxygen atmosphere when illuminated, and the original color recovery under heating condition.
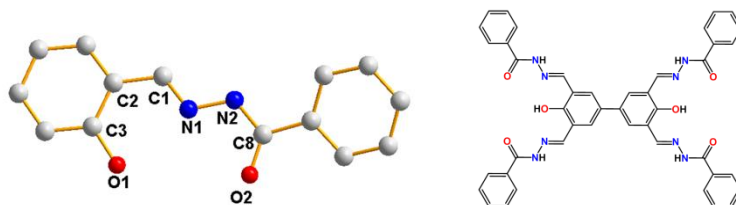

Supplementary Figure 7. The crystal structure of monomer model N'-(2-Hydroxybenzylidene)benzohydrazide and the structure of monomer model N',N'',N''',N''''-((1E,1'E,1''E,1'''E)-(4,4'-dihydroxy-[1,1'- biphenyl]-3,3',5,5'- tetrayl) tetrakis (methanylidene)) tetra (benzohydrazide).
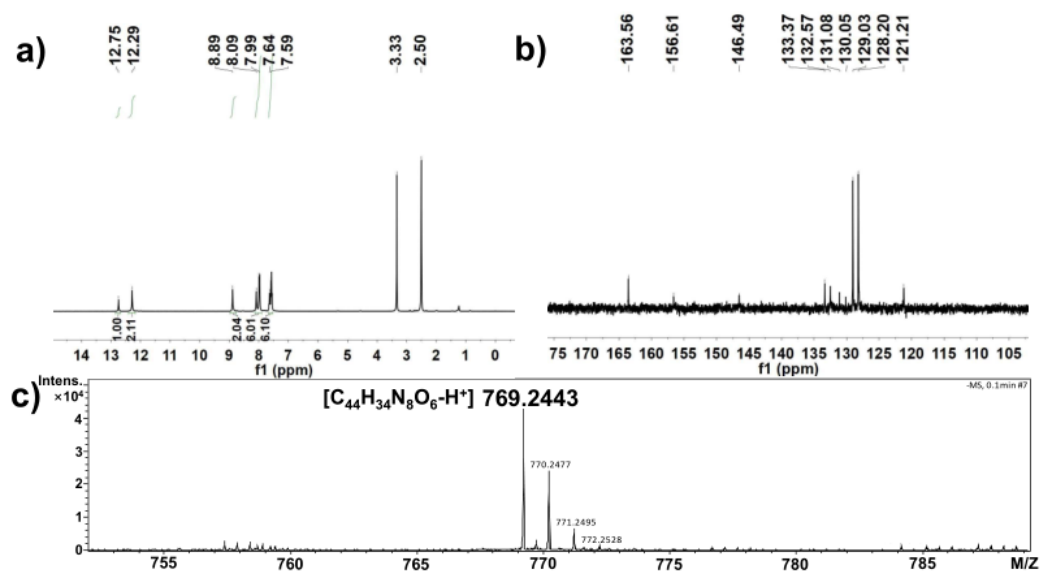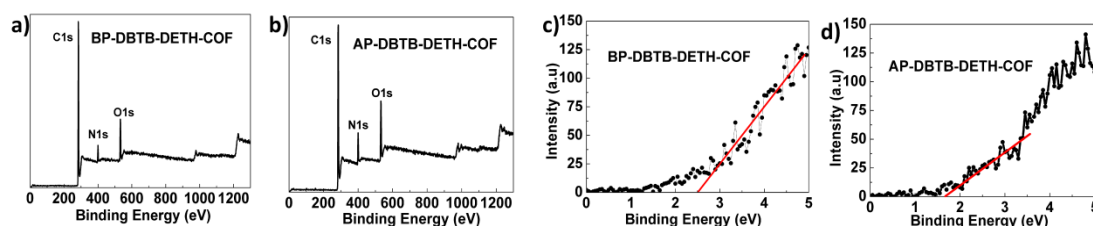
Supplementary Figure 8. The characterization of N',N'',N''',N''''-((1E,1'E,1''E,1'''E)-(4,4'-dihydroxy-[1,1'-biphenyl]-3,3',5,5'-tetrayl) tetrakis (methanylidene)) tetra (benzohydrazide) **a)** ^{1}H NMR, **b)** ^{13}C NMR and **c)** ESI-MS.
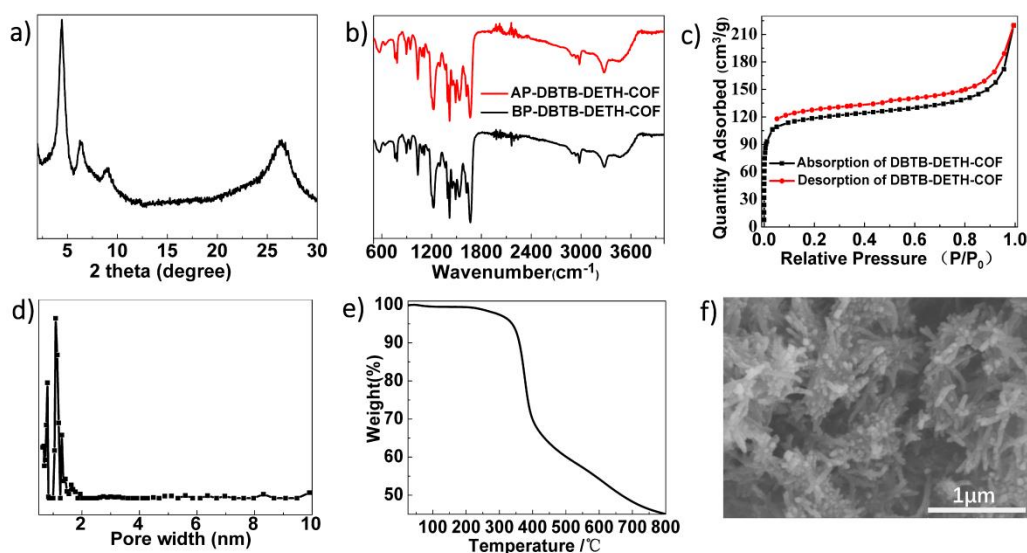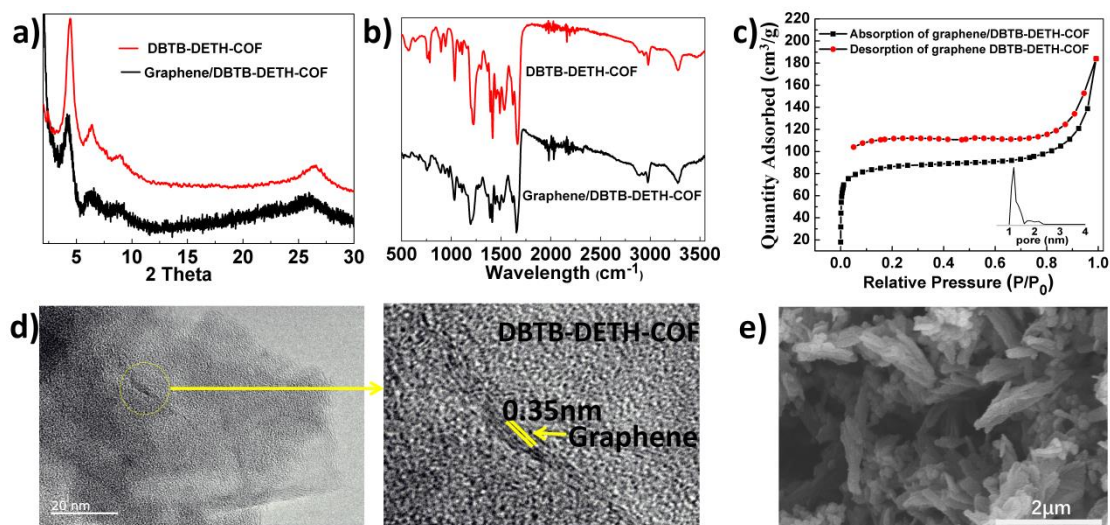

Supplementary Figure 9. The characterization of DBTB-DETH-COF after 15 days of light exposure (at this moment DBTB-DETH-COF is equivalent to AP-DBTB-DETH-COF). **a)** PXRD pattern of DBTB-DETH-COF under light for 15 days. **b)** FT-IR spectra of DBTB-DETH-COF under light for 15 days. **c)** BET of DBTB-DETH-COF under light for 15 days. **d)** pore-size distribution DBTB-DETH-COF under light for 15 days. **e)** TGA of DBTB-DETH-COF under light for 15 days. **f)** SEM images of DBTB-DETH-COF under light for 15 days.
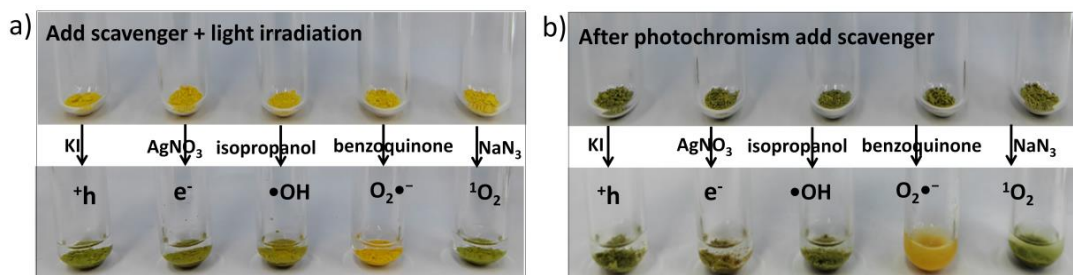
Supplementary Figure 10. quenching experiments. **a)** The color change of BP-DBTB-DETH-COF adding different quenching agents and illumination and **b)** AP-DBTB-DETH-COF adding different quenching agents.

Supplementary Figure 11. XPS spectra. **a** and **b)** The XPS spectra of before and after photochromism of DBTB-DETH-COF and **c** and **d**) XPS valance band spectra of before and after photochromism.

Supplementary Figure 12. The characterization of Graphene/DBTB-DETH-COF. **a)** PXRD pattern of DBTB-DETH-COF and Graphene/DBTB-DETH-COF. **b)** FT-IR spectrum of DBTB-DETH-COF and Graphene/DBTB-DETH-COF. **c)** BET of DBTB-DETH-COF at 77 K. The inset shows the pore-size distribution. **d)** The TEM of Graphene/DBTB-DETH-COF. **e)** SEM images of Graphene/DBTB-DETH-COF.