Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Visible Ozone Detection and Removal in Two-Dimensional Mn(II)-Based Metal-Organic Frameworks

Chen Dong[ab], Tao He[a], Wei Wu[a], Guang-Rui Si[a], Lin-Hua Xie,*[a] Jian-Rong Li[a]

[a] Beijing Key Laboratory for Green Catalysis and Separation and Department of Chemical Engineering, Beijing University of Technology, Beijing 100124, China.

[b] National Engineering Research Center for Rare Earth, Grirem Advanced Materials Co., Ltd., Beijing 100088, China.

E-mail: xielinhua@bjut.edu.cn

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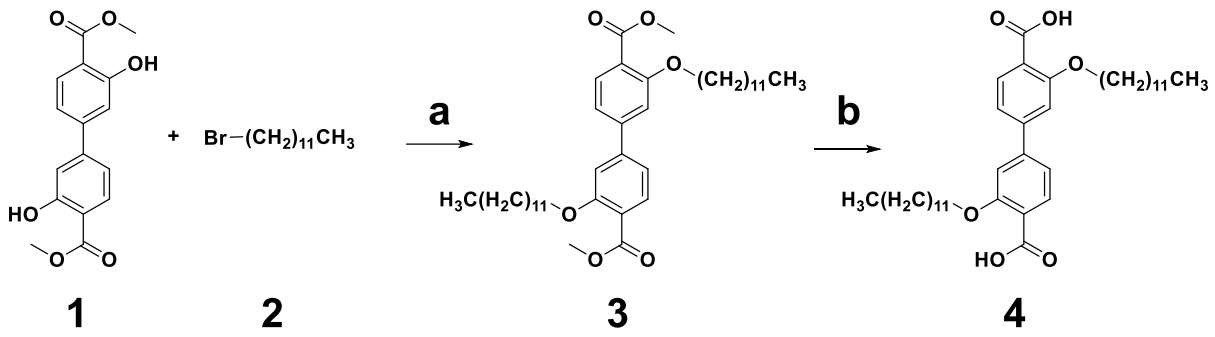
Section 1. Chemicals and Instruments

All general reagents and solvents were commercially purchased used as received without further purification unless otherwise noticed. Manganese chloride tetrahydrate ($MnCl_2·4H_2O$), methanol (MeOH), alcohol (EtOH), 1-Bromododecane, 1-Bromohexadecane, and 1-Bromoicosane were purchased from Beijing InnoChem Science & Technology Co., Ltd. Potassium carbonate (K_2CO_3), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Beijing Chemical Reagent Company. *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), and hydrazine hydrate (50%) were bought from Sinopharm Chemical Reagent Co. Ltd. 4-watt UV lamp was bought from Beijing Aerospace HONGDA Optoelectronics Technology Co. Ltd. O_3 monitor (Model 205) was bought from 2B Technologies. Humidity generator (HSDG-A) was bought from Suzhou Huaxiangshida Environmental Protection Technology Co., Ltd.

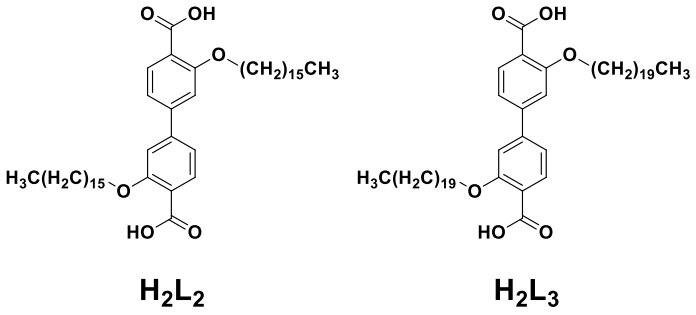
The powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Smartlab3 X-ray Powder Diffractometer equipped with a Cu-sealed tube (λ = 1.54178 Å). N_2 adsorption/desorption isotherms were measured by using a BELSORP MAX II Surface Characterization Analyzer at 77 K. ^{1}H NMR data were recorded on a Bruker Avance 400 MHz spectrometer. An IR Affinity-1 instrument was used for recording Fourier transform infrared (FT-IR) spectra. Thermogravimetric analysis (TGA) data were obtained on a TGA-50 (Shimadzu) thermogravimetric analyzer with heating from 25 to 800 °C (10 °C min^{-1}) under air atmosphere. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCALAB 250 instrument. The water contact angles were measured on the contact angle system JY-82C (Chengde Dingsheng, China).

Section 2. Experimental Section



Scheme S1. Synthetic procedure for H_2L_1.

Synthesis of H_2L_1. Dimethyl 3,3′-dihydroxy-[1,1′-biphenyl]-4,4′-dicarboxylate (**1**, 302 mg, 1 mmol), 1-Bromododecane (**2**, 623 mg, 2.5 mmol), K_2CO_3 (276 mg, 2 mmol) and DMF (5 mL) were added to a 50 mL one-neck flask equipped with a condenser. The reaction mixture was heated to 85 °C and stirred for 3 h. After cooling to room temperature, the reaction mixture was concentrated in vacuo to remove a portion of the DMF. After that a mixed solution of methanol (10 mL), THF (10 mL), and NaOH solution (10 mL, 2 M) was added. The mixture was heated to 80 °C and stirred for 8 hours. The THF and MeOH were evaporated, and then dilute HCl was added to the remaining aqueous solution until the solution was at pH =3. The solid was collected by filtration, washed with water, and dried to give the final product as white solid (H_2L_1, **4**). ^{1}H NMR (400MHz, DMSO-d_6) δ: 7.71 (d, 1H), 7.35-7.31(m, 2H), 4.16 (t, 2H), 1.74 (m, 2H), 1.46 (m, 2H), 1.24 (m, 12H), 0.87-0.83 (d, 4H).



Scheme S2. H_2L_2 and H_2L_3 ligands.

Synthesis of H_2L_2. The synthetic method of H_2L_2 is similar to that of H_2L_1, except that compound **2** was replaced by 1-bromohexadecane. The product is a light pink solid (Scheme S2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (d, 1H), 7.35 (d, 1H), 7.24 (s, 1H), 4.36 (t, 2H), 1.99 (m, 2H), 1.54 (m, 2H), 1.41 (m, 2H), 1.27 (m, 18H), 0.89 (t, 4H)

Synthesis of H_2L_3. The synthetic method of H_2L_3 is similar to that of H_2L_1, except that compound **2** was replaced by 1-bromoicosane. The product is a white solid (Scheme S2). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (d, 1H), 7.36 (d, 1H), 7.22 (s, 1H), 4.36 (t, 2H), 1.99 (m, 2H), 1.54-1.28 (m, 24H), 0.89 (t, 10H).

Section 3 Crystallographic Data

Table S1. Crystal data and structural refinement of BUT-82 (CCDC number: 2277540).

Compound name	BUT-82
Empirical formula	$C_{76}H_{112}O_{12}Mn_2$
Formula weight	1327.53
Temperature (K)	293(4)
Crystal system	triclinic
Space group	*P*-1
a (Å)	7.7021(3)
b (Å)	22.3914(11)
c (Å)	23.6873(16)
α (°)	112.516(5)
β (°)	90.520(4)
γ (°)	99.496(4)
V (Å^3)	3710.3(4)
Z	2
Calculated density (g/cm^3)	0.941
F(000)	4720.0
μ/mm^{-3}	3.125
Reflections collected	45260
Independent reflections	8702 [*R*(int) = 0.0997]
Goodness-of-fit on F^2	0.967
Final *R* indices [$I > 2\sigma(I)$]	R_1[a] = 0.1303, wR_2[b] = 0.3258
R indices (all data)	R_1 = 0.1631, wR_2 = 0.3550
Largest diff. peak and hole (e/Å^3)	2.331/-0.857

[a] $R_1 = \Sigma(||F_0|-|F_C||)/\Sigma|F_0|$.

[b] $wR_2 = [\Sigma w(|F_0|^2-|F_C|^2)^2/\Sigma w(F_0^2)]^{1/2}$

Section 4 Supplementary Figures

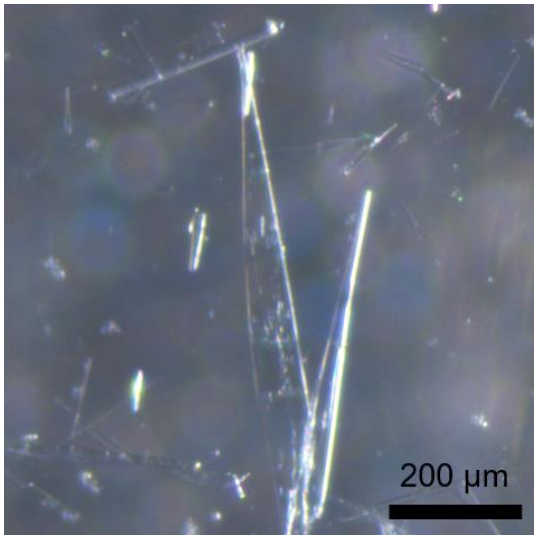


Figure S1. The image for BUT-82 single crystal under an optical microscope.

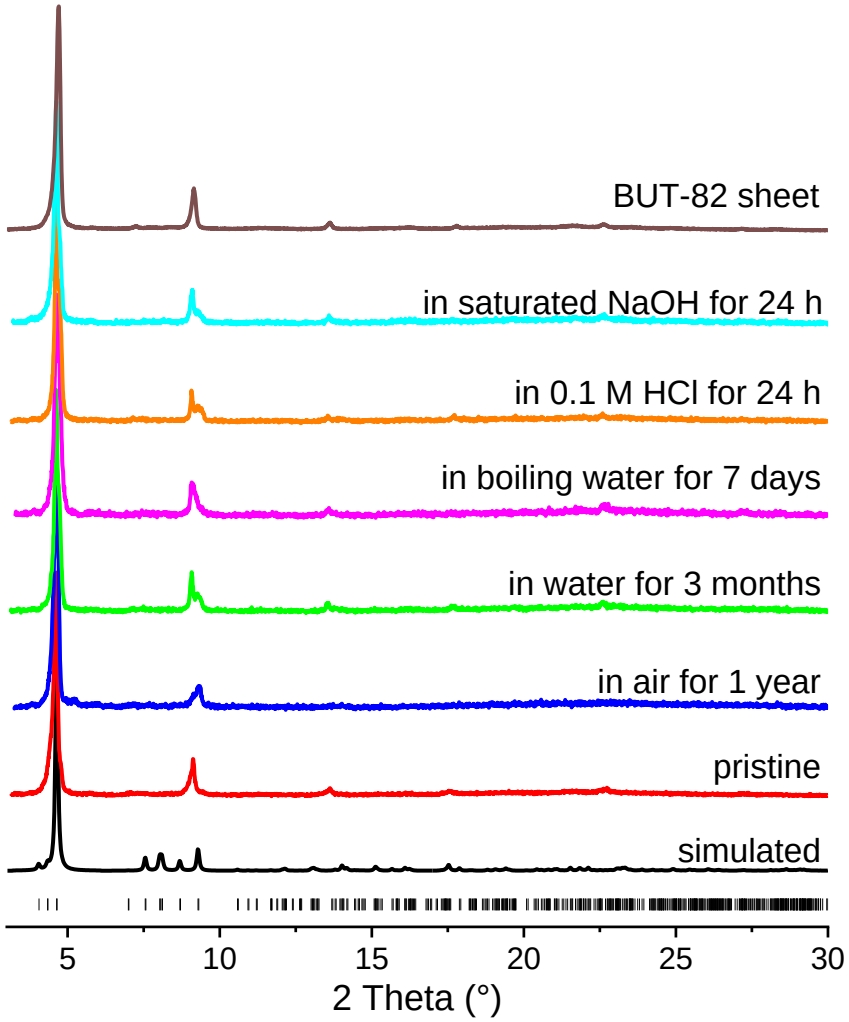


Figure S2. PXRD patterns of BUT-82 samples treated under different conditions.

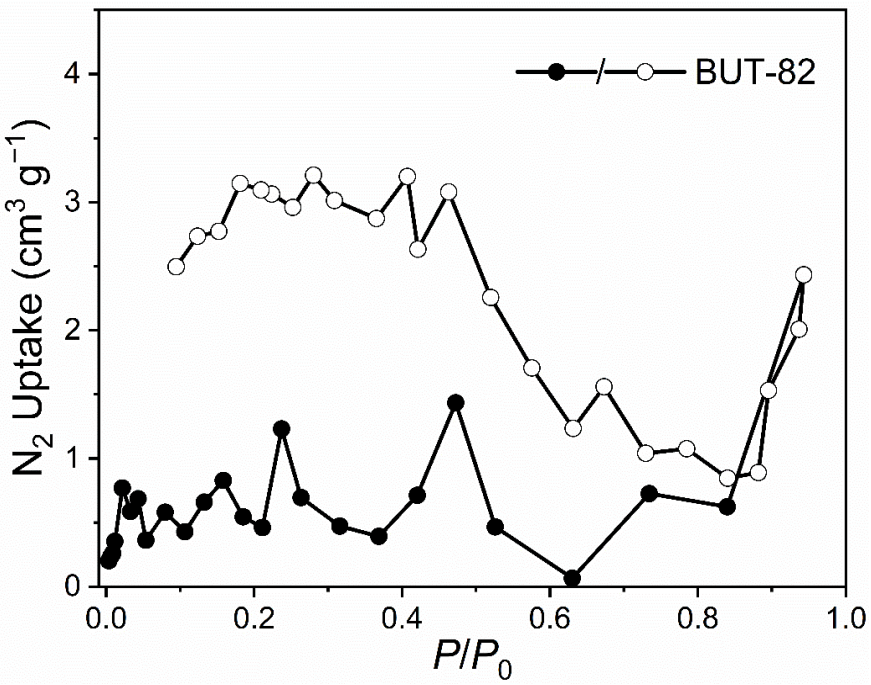


Figure S3. (a) N_2 adsorption/desorption isotherms at 77 K for BUT-82.

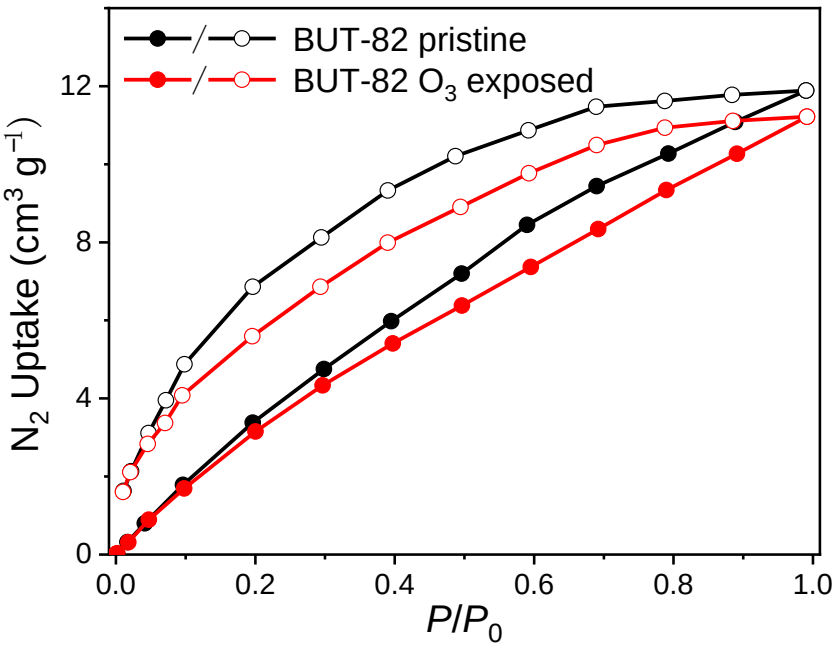


Figure S4. (a) CO_2 adsorption/desorption isotherms of pristine and O_3 exposed BUT-82 at 195 K.

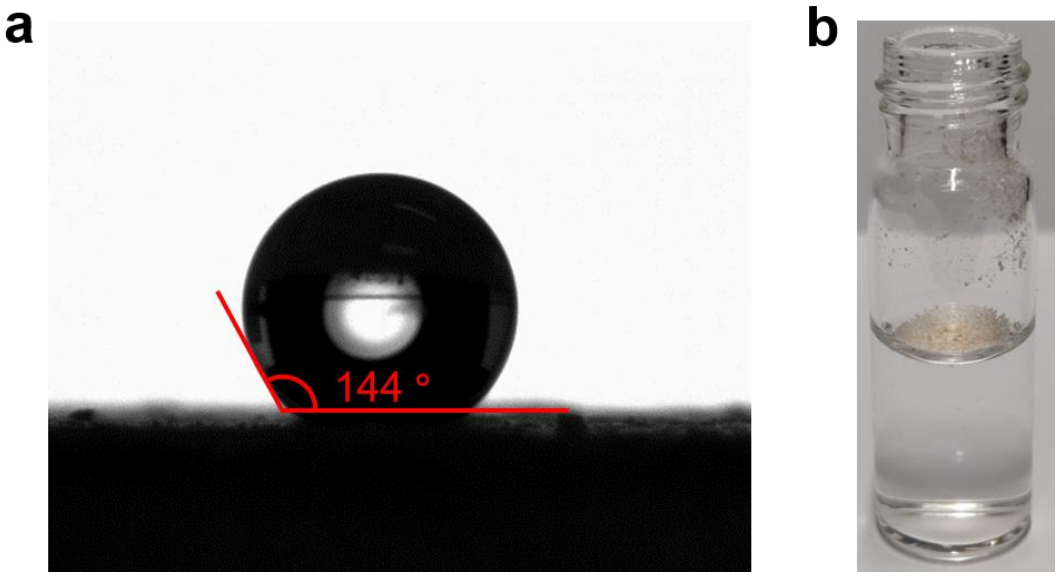


Figure S5. The static water contact angle of BUT-82. (b) The photo of BUT-82 crystals floating on the water surface.

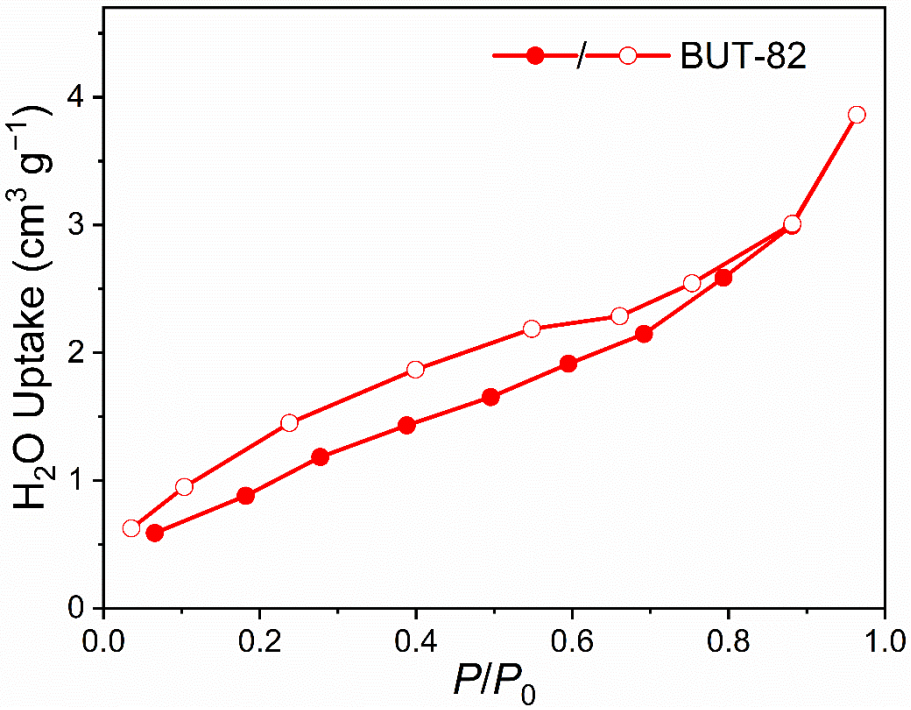


Figure S6. Water adsorption/desorption isotherms at 298 K for BUT-82.

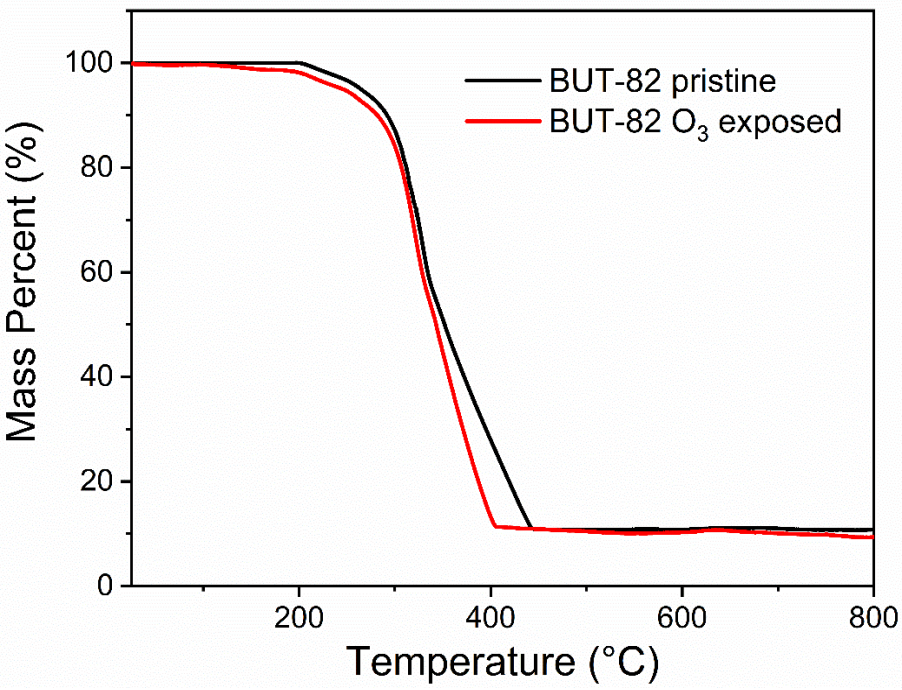


Figure S7. The TGA curves of pristine and O_3 exposed BUT-82 samples recorded under air flow.

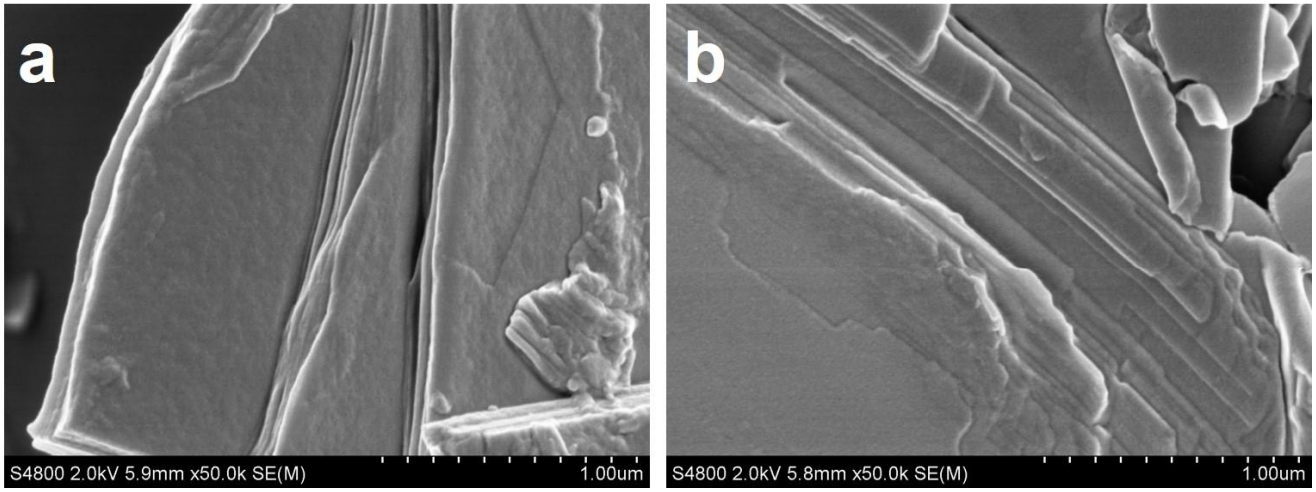


Figure S8. SEM images of a) pristine and b) O_3 exposed BUT-82.

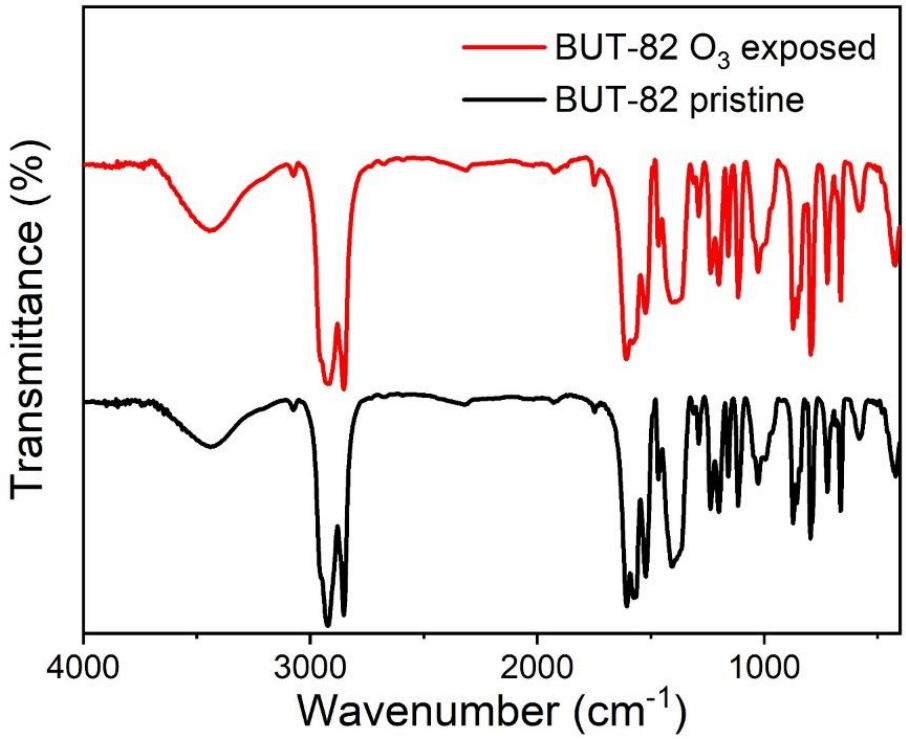


Figure S9. The FT-IR spectra of pristine and O_3 exposed BUT-82 samples.

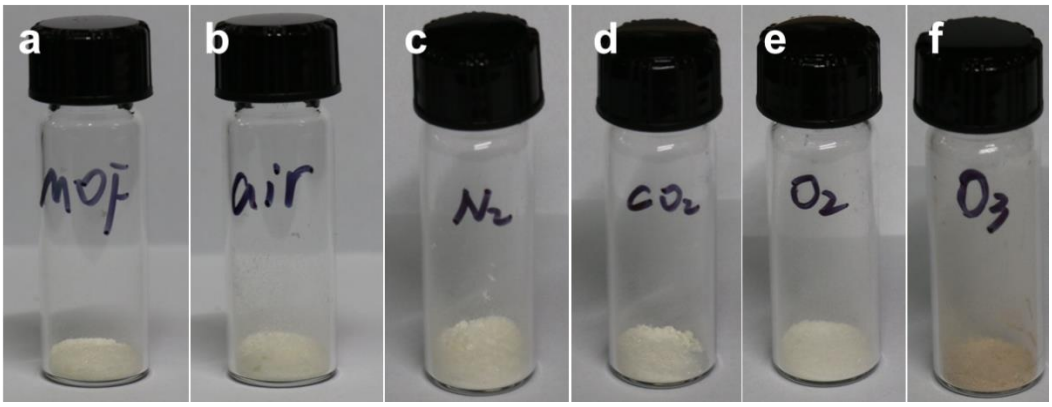


Figure S10. Photographs of the color changes observed for BUT-82 treating with different gases for 30 min. (a) pristine BUT-82; (b) air; (c) N_2; (d) CO_2; (e) O_2; (f) O_3.

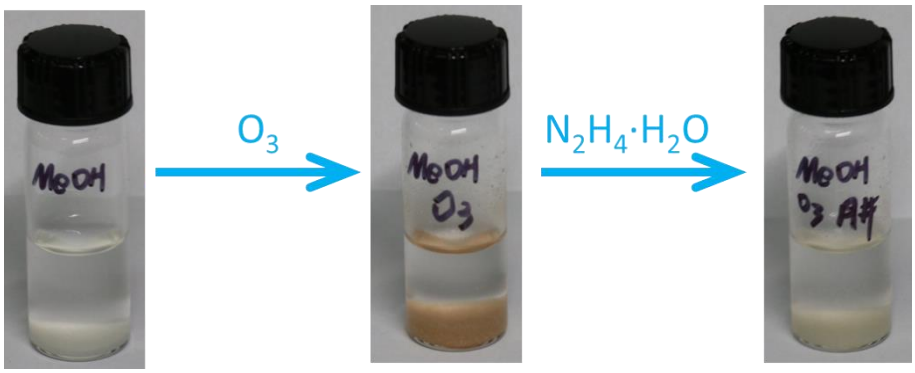


Figure S11. Photographs of BUT-82 dispersed in MeOH after O_3 and subsequent $N_2H_4 \cdot H_2O$ vapor bubbling treatment, respectively.

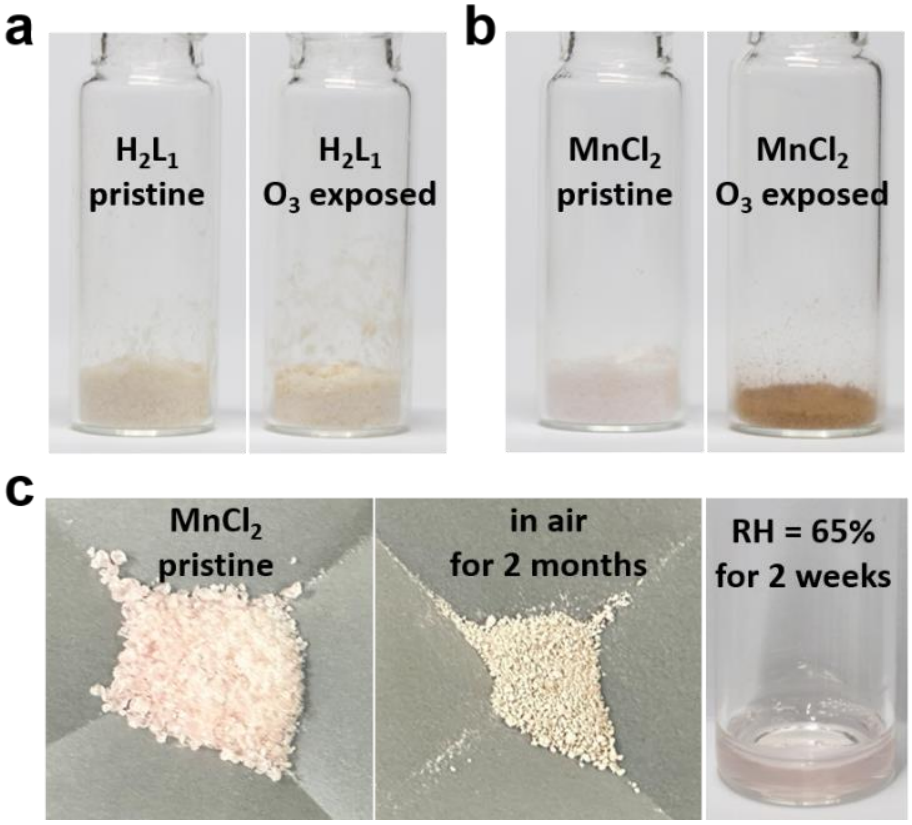


Figure S12. (a) H_2L_1 ligand and (b) $MnCl_2 \cdot 4H_2O$ after 10 min of 10 ppm O_3 purging. (c) Changes of color and state of $MnCl_2 \cdot 4H_2O$ after placing in air or high humidity environment.

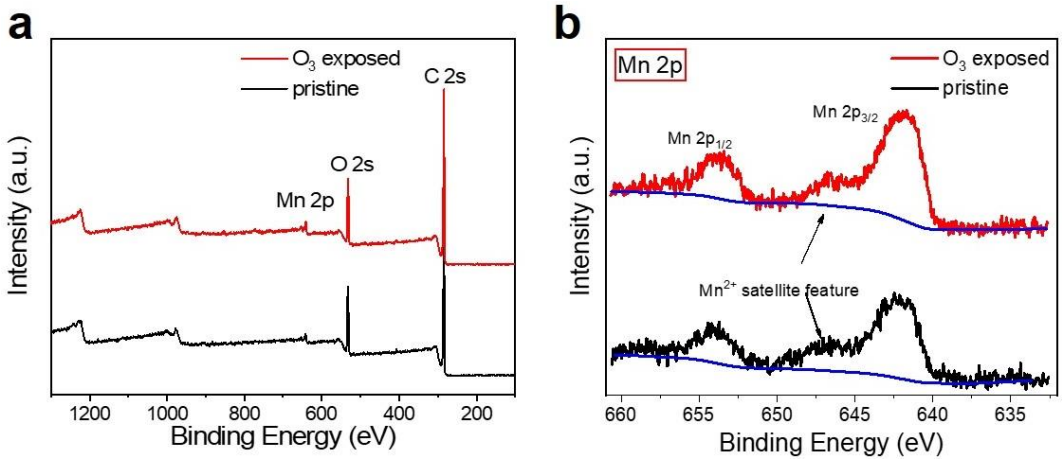


Figure S13. The XPS (a) survey and (b) Mn 2p spectra of pristine and O_3 exposed BUT-82 samples.

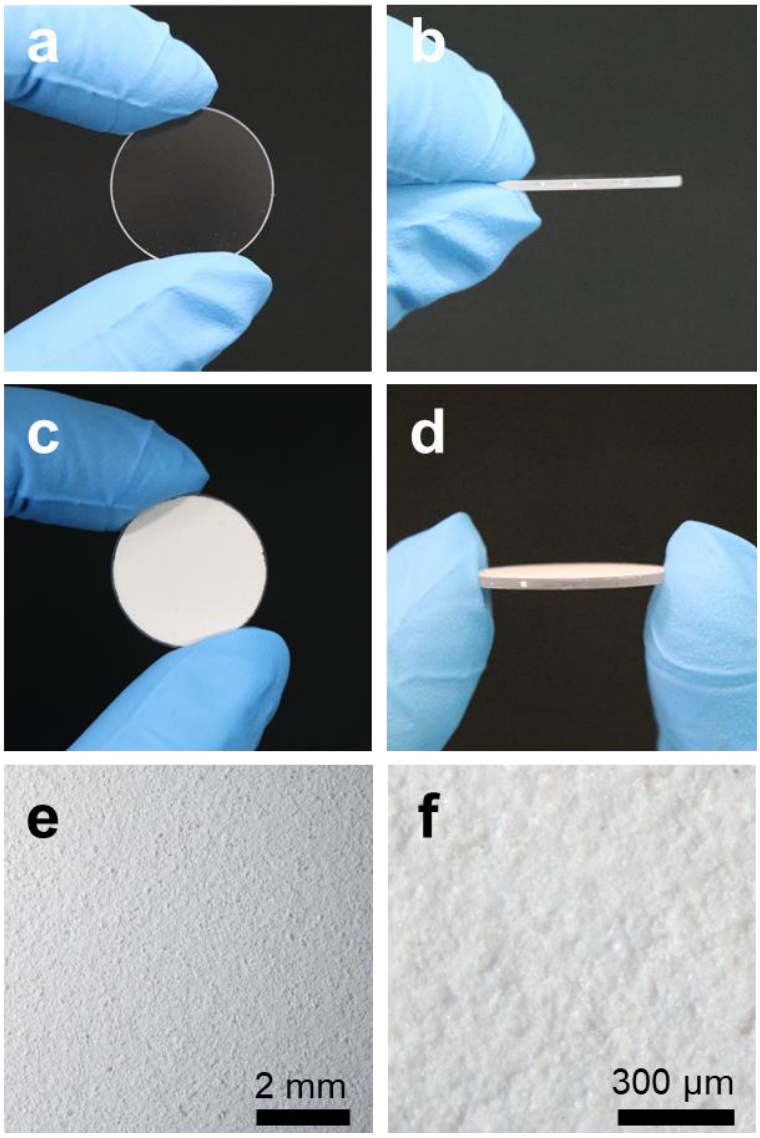


Figure S14. Photographs of (a, b) blank quartz wafer and (c, d) BUT-82 film. (e, f) Images of the BUT-82 film under an optical microscope.

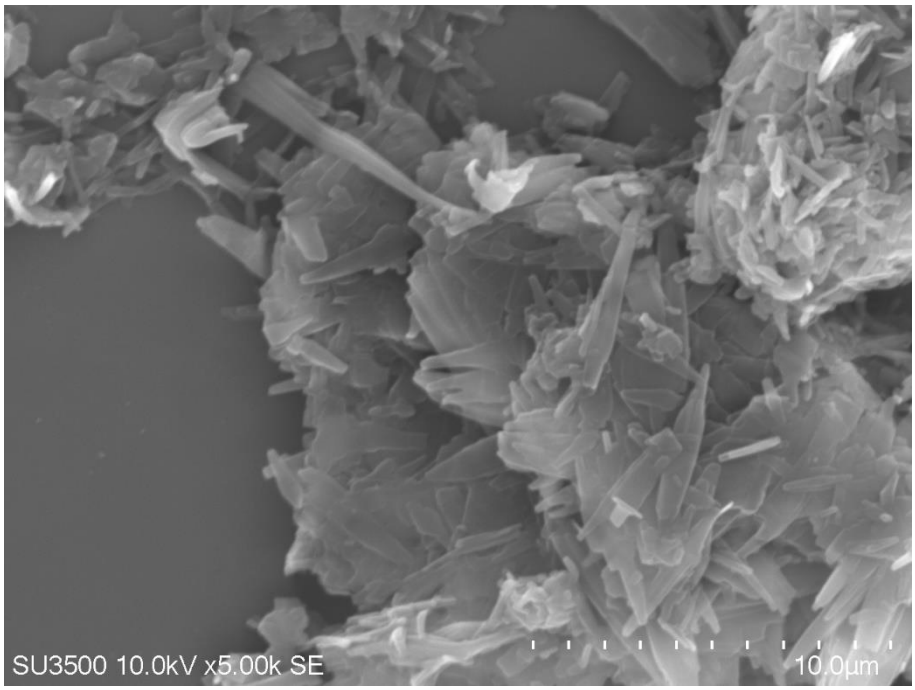


Figure S15. The SEM image for BUT-82 microcrystal.

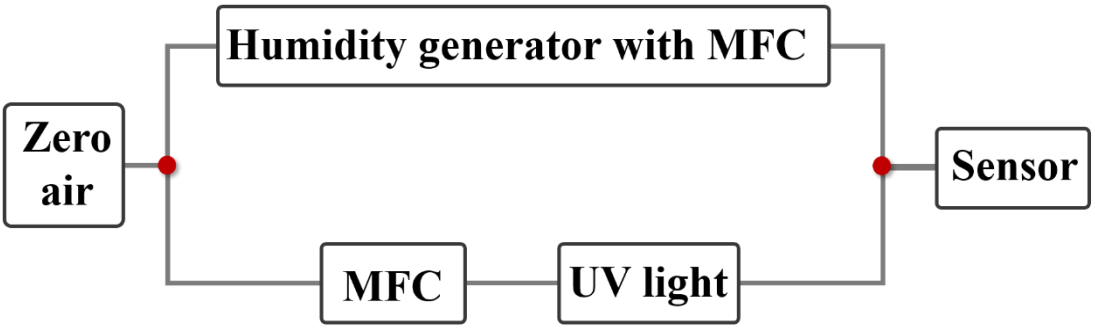


Figure S16. The schematic of the setup for O_3 sensing test.

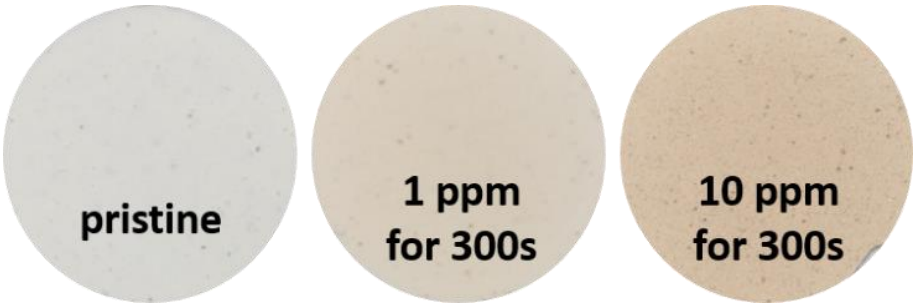


Figure S17. Photographs of BUT-82 films after 300s of O_3 purging with different concentrations at 50% RH.

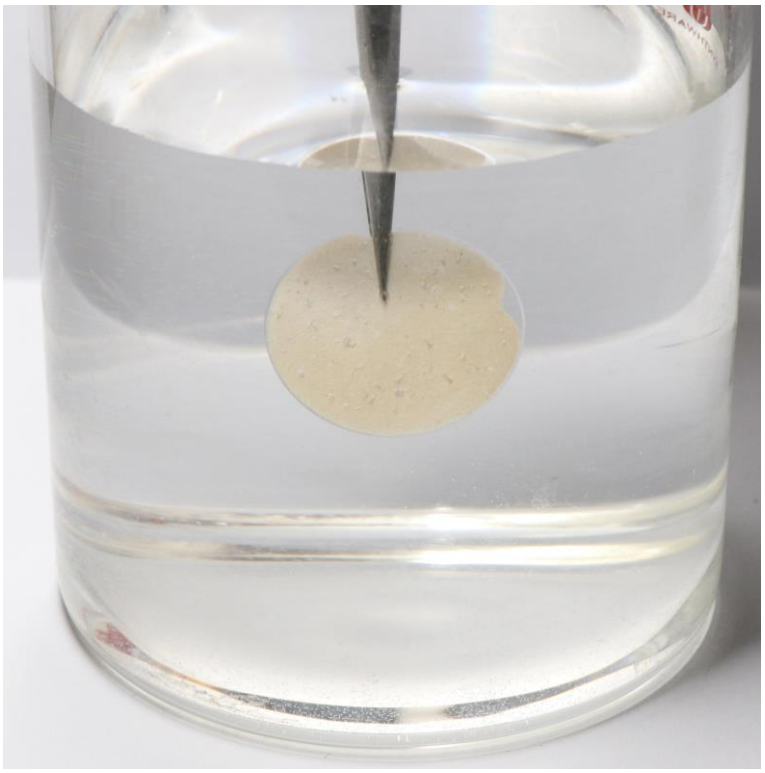


Figure S18. The photograph of the BUT-82 film in H_2O after O_3 bubbling treatment.

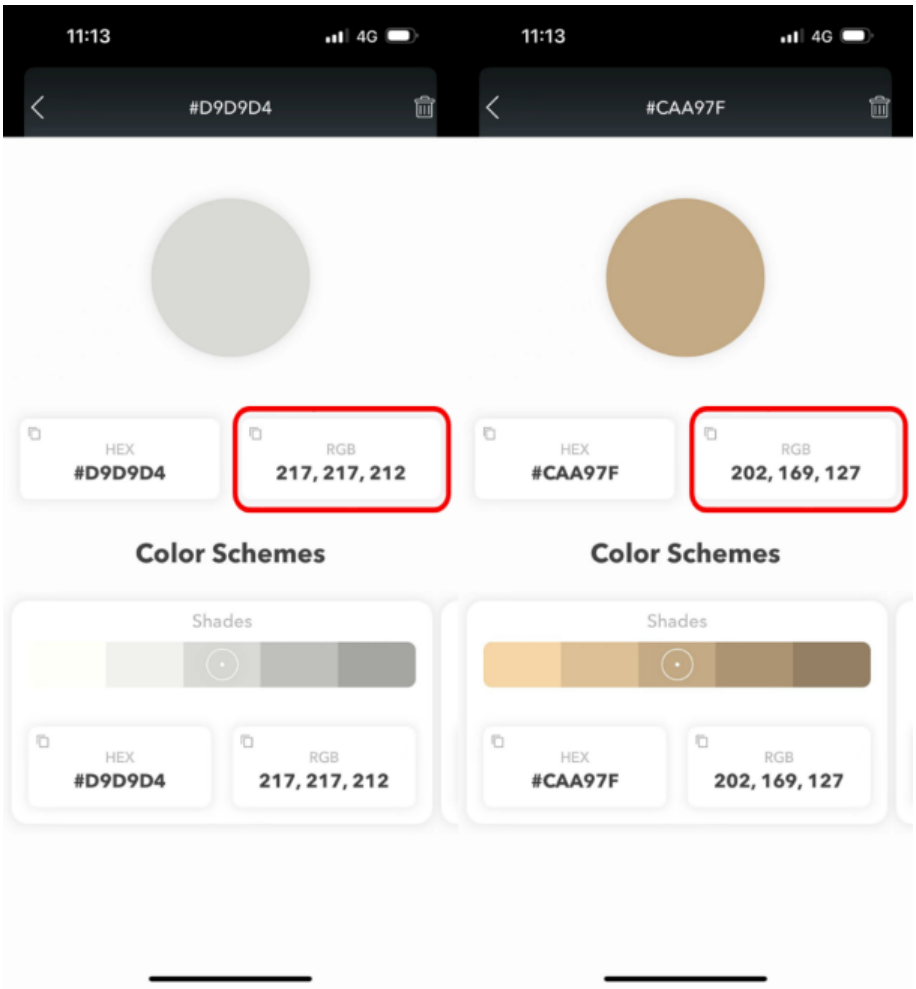


Figure S19. The color recognition software on the smart phone.

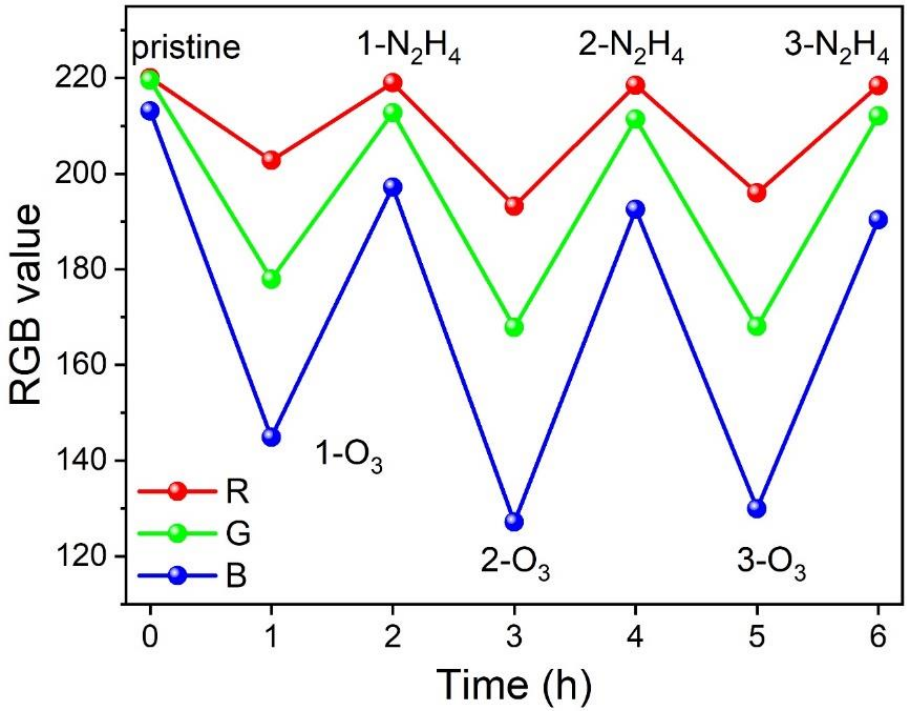


Figure S20. RGB values response of BUT-82 films in the cycle test of O_3 sensing.

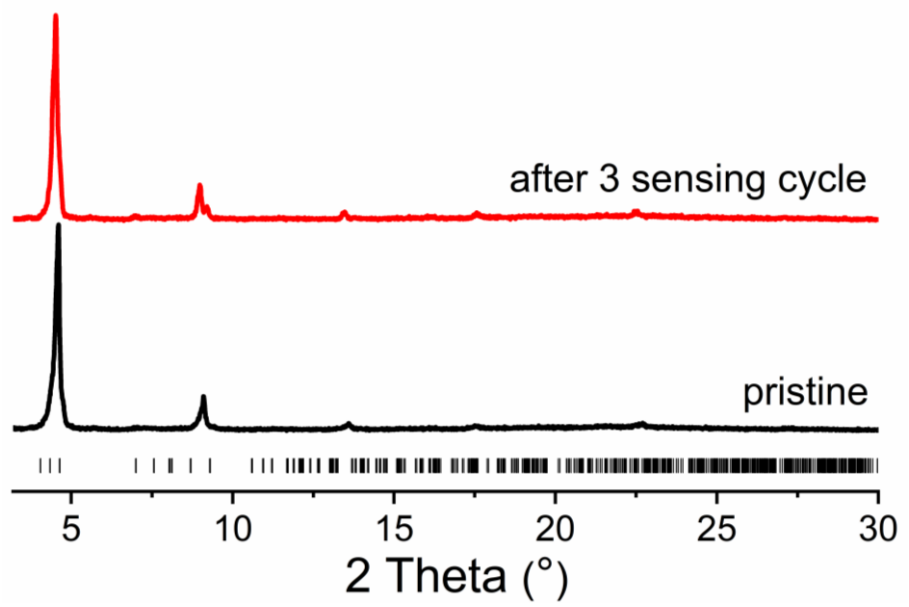


Figure S21. PXRD patterns of the BUT-82 film before and after the cycle test of O_3 sensing.

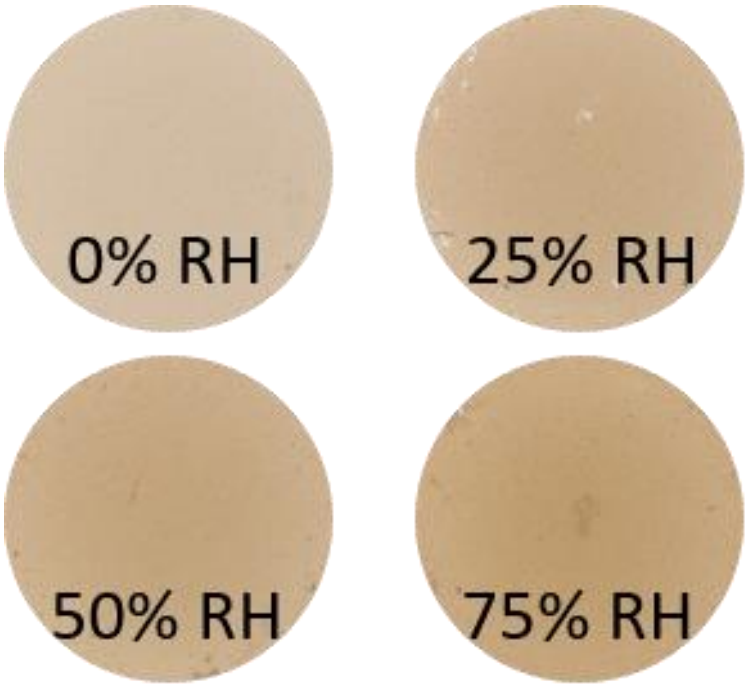


Figure S22. Photographs of BUT-82 films after 60 min of 50 ppm O_3 purging at various humidity levels.

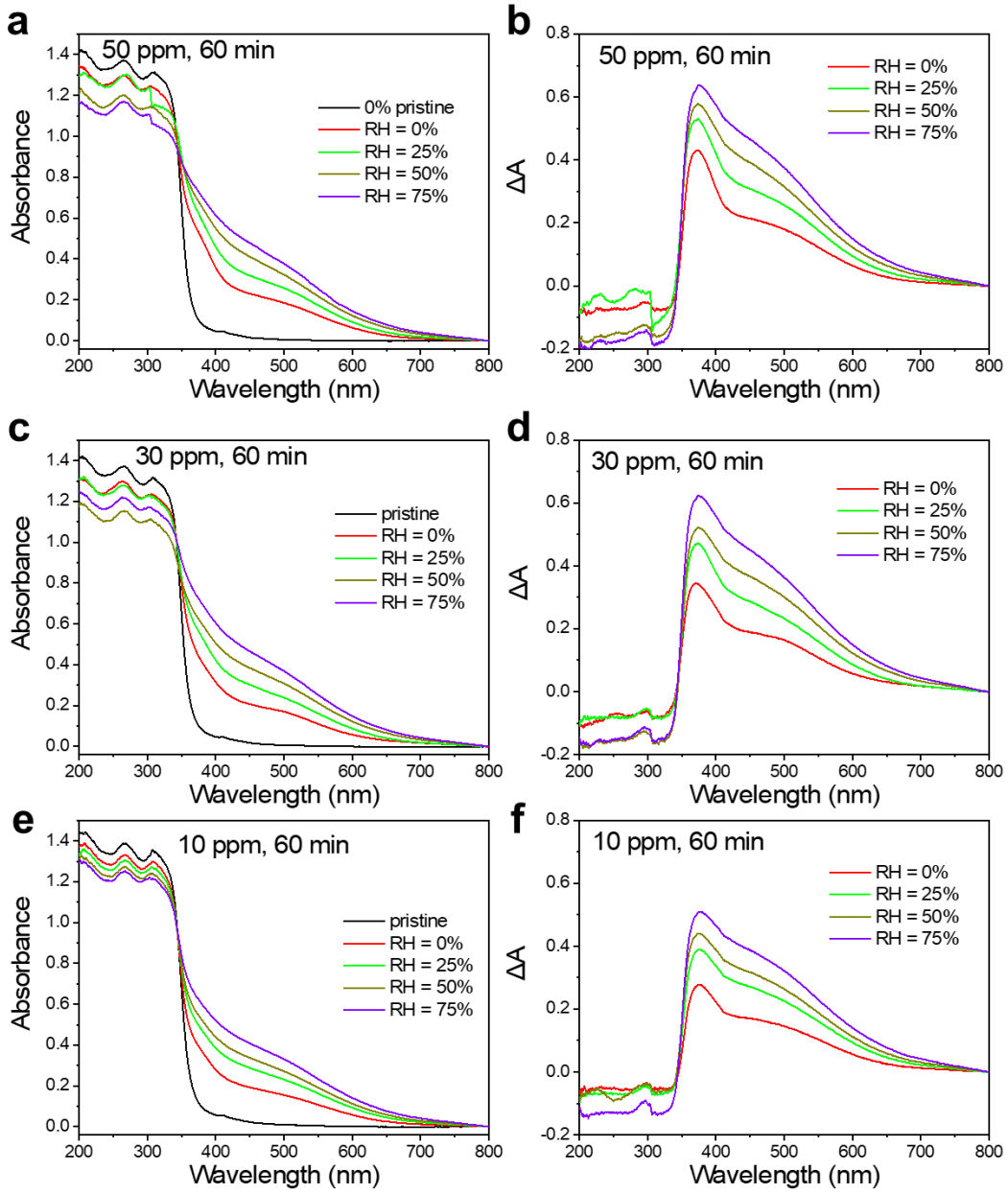


Figure S23. UV/Vis spectra and absorption difference of BUT-82 films after O_3 purging with various concentrations under different relative humidity levels. (a, b) 50 ppm, (c, d) 30 ppm, and (e, f) 10 ppm.

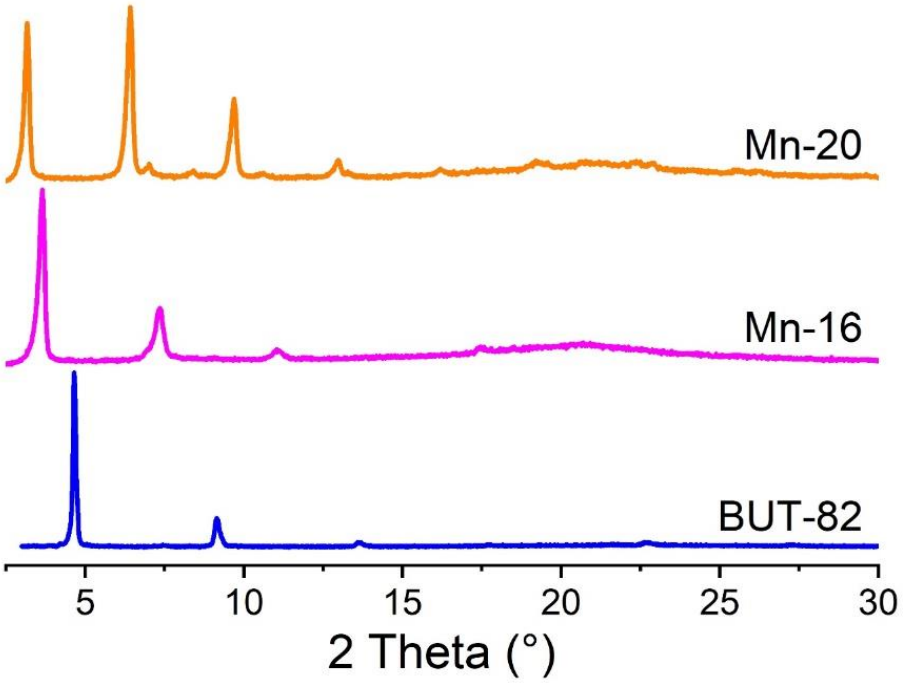


Figure S24. PXRD patterns of BUT-82, Mn-16, and Mn-20 samples.

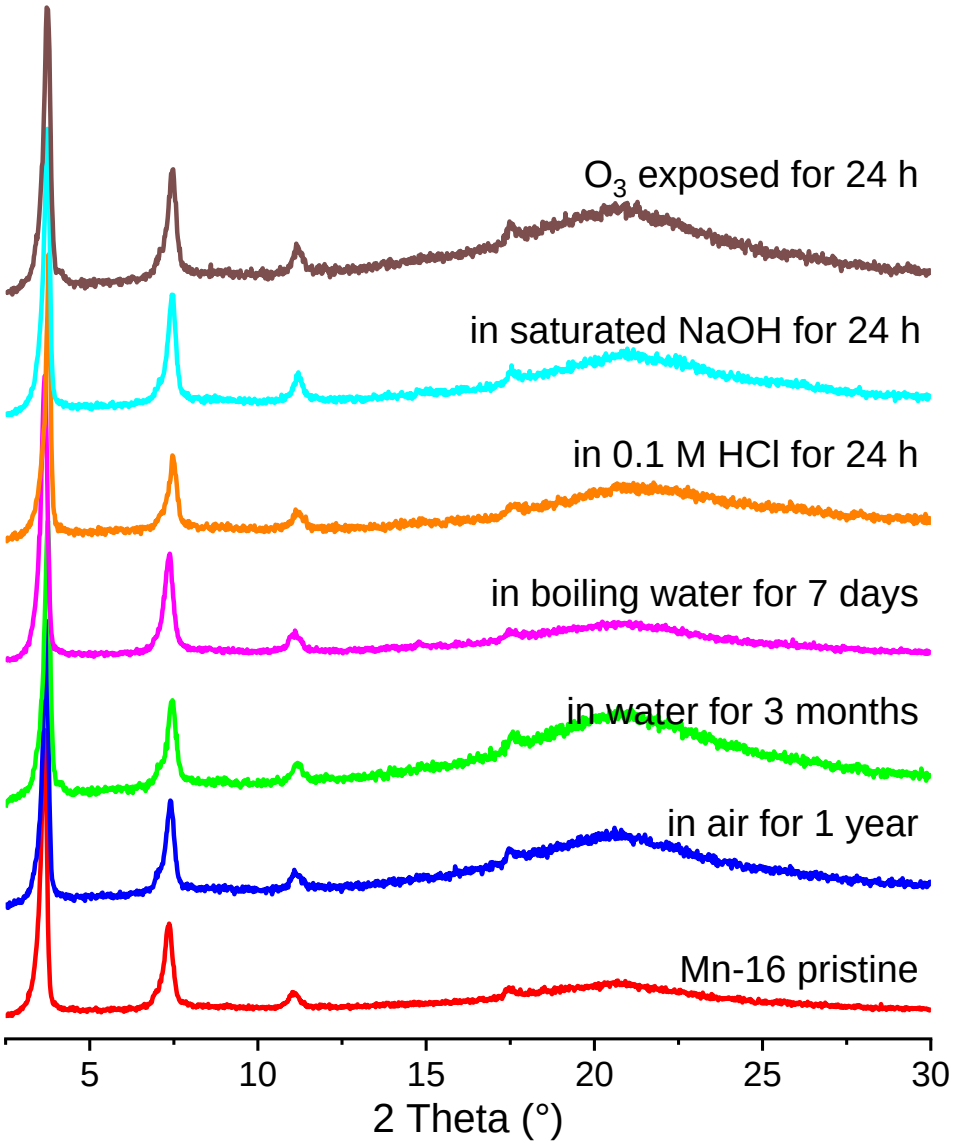


Figure S25. PXRD patterns of Mn-16 samples treated under different conditions.

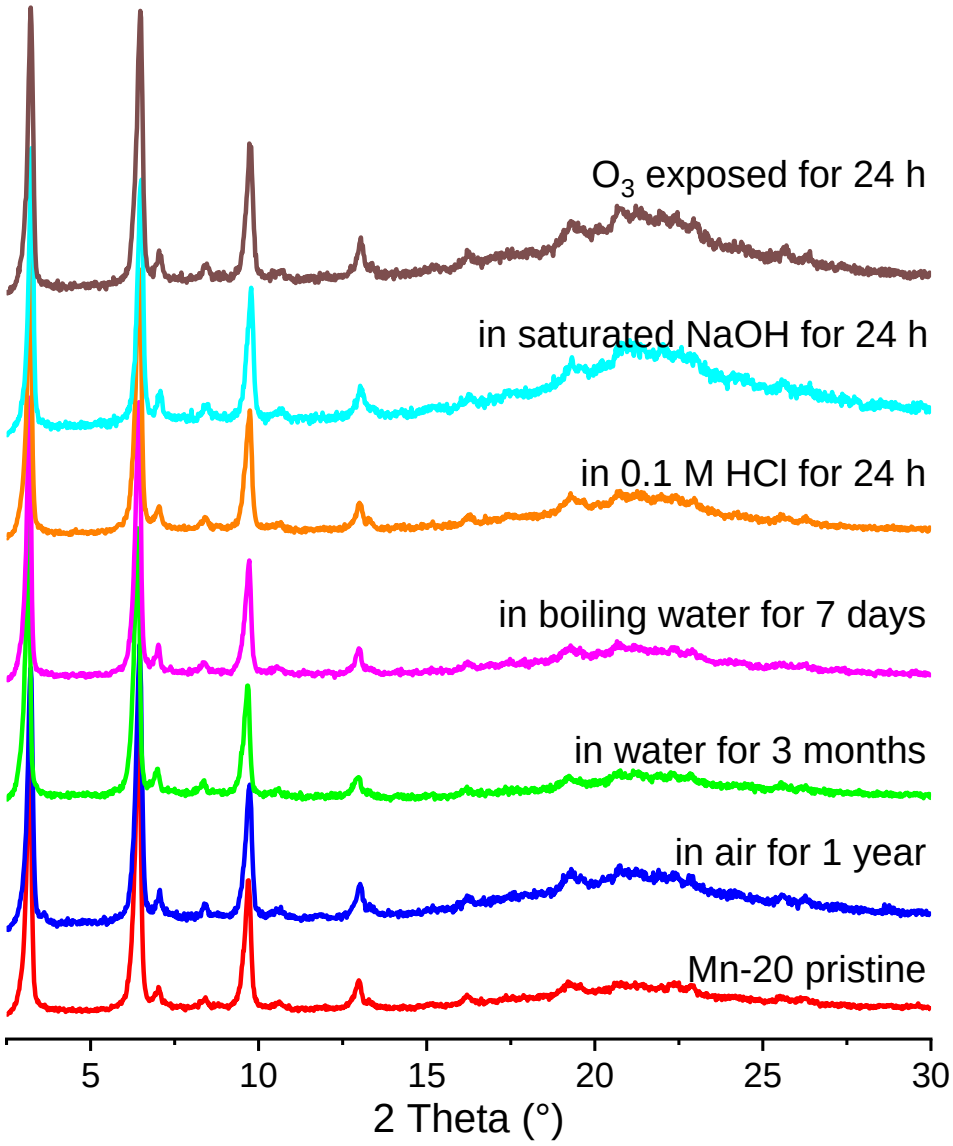


Figure S26. PXRD patterns of Mn-20 samples treated under different conditions.

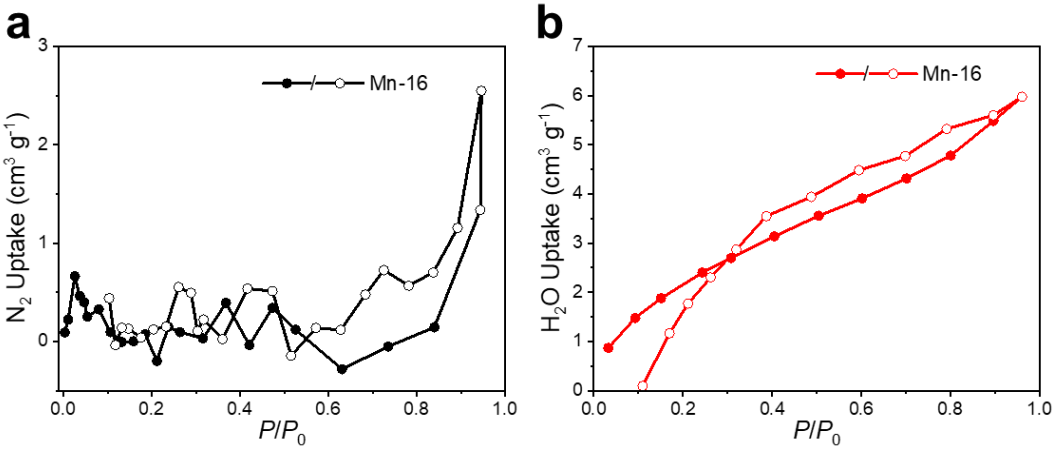


Figure S27. (a) N_2 adsorption/desorption isotherms at 77 K and (b) water adsorption/desorption isotherms at 298 K of Mn-16.

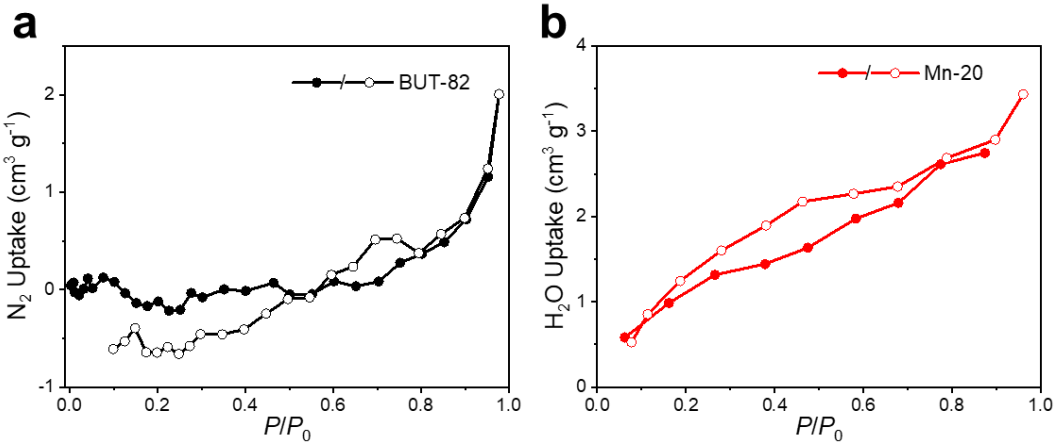


Figure S28. (a) N_2 adsorption/desorption isotherms at 77 K and (b) water adsorption/desorption isotherms at 298 K of Mn-20.

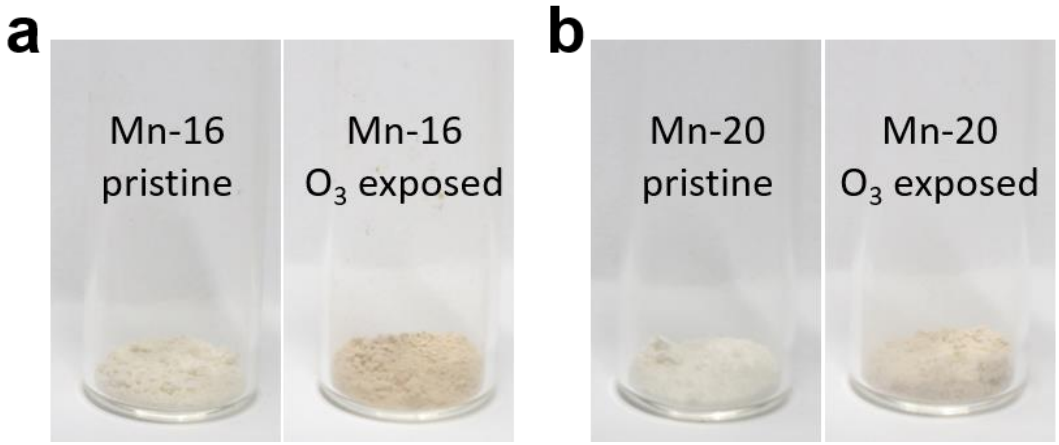


Figure S29. Photographs of pristine and O_3 exposed (a) Mn-16 and (b) Mn-20 samples.

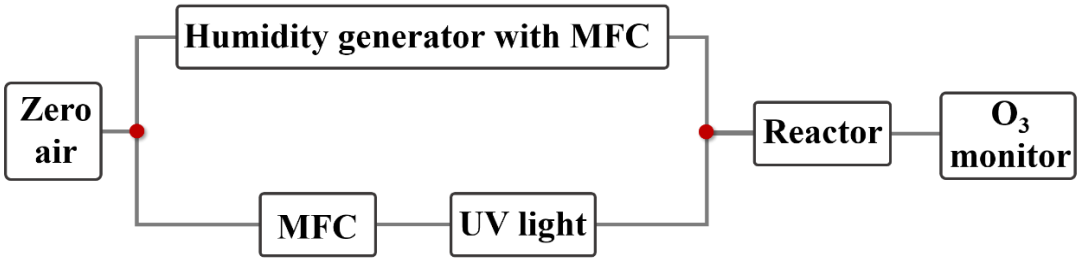


Figure S30. The schematic of the setup for O_3 decomposition test.

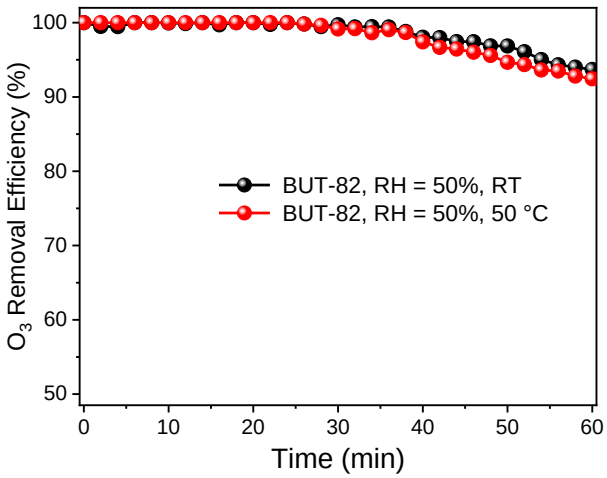


Figure S31. The O_3 removal efficiencies for BUT-82. Other test conditions: 0.02 g test substance diluted with 0.4 g quartz sand, concentration of O_3 = 1 ppm, flow rate = 0.5 L min^{-1}, RT or 50 °C.