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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The present manuscript reports the synthesis of a hydrazone-linked DBTB-DETH-COF. This COF was found to exhibit reversible photochromism, changing from yellow to olive in the presence of light and air, and reverting to the original color upon heating. It can be utilized as an anti-counterfeiting ink and optical switch in the presence of air. I believe the work has been well executed, and the paper is generally well-written. The content of this study is suitable for publication in Nature Communications as an article. However, there are still some issues that need to be addressed. Therefore, I could recommend acceptance of the paper in this journal after the following minor revisions:

1. The experiment of exposing the COF to light in a pure oxygen environment should be done to eliminate the interference of other components in the air, such as water.
2. The XRD peaks of BTB-DETH-COF, aside from the main peak, do not align well with the simulated PXRD pattern.
3. Please provide the PXRD of AP-DBTB-DETH-COF.
4. Labels “b” and “c” in Fig. 7 do not correspond to the legend below the Figure.
5. In line 51, the wavelength of C=N linkage is referred to 1620 cm^{-1} , but in Supplementary Figure 1a, it is referred to 1665 cm^{-1} .

Reviewer #2 (Remarks to the Author):

The manuscript reports a COF with photochromic property. This is a new type of materials.

1. The introduction is relatively short. A slightly broader background would be instructive for the readers.
2. How about photochromic property of DBTB itself or a model compound? What is the advantage of COF?
3. In Figure 5, there is a small peak at 533 eV for AP sample. This fitting is wrong. The FWHM of the peak should follow certain rule.

4. The mechanism of photochromic is elusive. In line 83, the new adsorption bands for AP COF sample is ascribed to PET. In line 99, The photochromic is ascribed to radicals. What kind of radical? Generally, the radical is short-lived.

5. There are many grammatic errors and typos in the manuscript.

Reviewer #3 (Remarks to the Author):

In this manuscript, a reversible photochromic hydrazone-linked COF DBTB-DETH-COF was reported. It showed an interesting reversible photochromism from yellow to olive in the presence of light and air, and back to the original color upon heating. Additionally, the related reason of photochromic process was discussed by various techniques and measurements. Furthermore, it was used as anti-counterfeiting ink and optical switch. Considering that there are rarely relevant reported on COFs photochromism, this work is quite of interest and novelty. It would expand the applications of COFs. Thus, I suggest its acceptance subject to some revisions, as listed in the below:

1. As for the synthesis of DBTB-DETH-COF, the ultrasonic method was employed and revealed several advantages in comparison to traditional solvothermal approach. However, some control experiments should be performed to confirm the real role of ultrasonic irradiation. Since 1 h ultrasound, the solvent mixture will be heated to a high temperature. Then, the synthesis should be performed only by heating without ultrasound. On the other hand, DBTB-DETH-COF sample is suggested to be prepared by solvothermal approach. And the as-synthesized sample should be compared with the sample from ultrasonic method in crystallinity, surface area, chemical stability and photochromism, in order to further confirm the advantages of ultrasonic method.
2. The experimental procedure for DBTB-DETH-COF photochromism should be added into the main article. Besides, a real time video for monitoring such photochromism from yellow to olive and back to yellow is suggested to be added as supplementary materials.
3. As for the mechanism of photochromism, authors attributed it to be caused by superoxide radicals which formed through electron transfer induced by photoexcitation. However, this superoxide radical is not stable and can not survive for a long time. Moreover, it is not olive color. Thus, the color change of DBTB-DETH-COF after photochromism should be caused by the change of COF itself. Then, which part of COF? And how did it back to yellow after heating? These things are not quite clear.
4. It is very interesting that Graphene/DBTB-DETH-COF composite material can be used as oxygen detecting sensor. So, can this device be used to quantitatively analyze the concentration of oxygen? Then, it would be more applicable for the practical applications.

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3. Please provide the PXRD of **AP-DBTB-DETH-COF**.

4. Labels “b” and “c” in Fig. 7 do not correspond to the legend below the Figure.

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superoxide radicals which formed through electron transfer induced by photoexcitation. However, this superoxide radical is not stable and can not survive for a long time. Moreover, it is not olive color. Thus, the color change of **DBTB-DETH-COF** after photochromism should be caused by the change of COF itself. Then, which part of COF? And how did it back to yellow after heating? These things are not quite clear.

4. It is very interesting that **Graphene/DBTB-DETH-COF** composite material can be used as oxygen detecting sensor. So, can this device be used to quantitatively analyze the concentration of oxygen? Then, it would be more applicable for the practical applications.

Point-by-point response to the referees' comments

Responds to the reviewer#1's comments:

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[Response: we appreciated such a positive comment very much!](#)

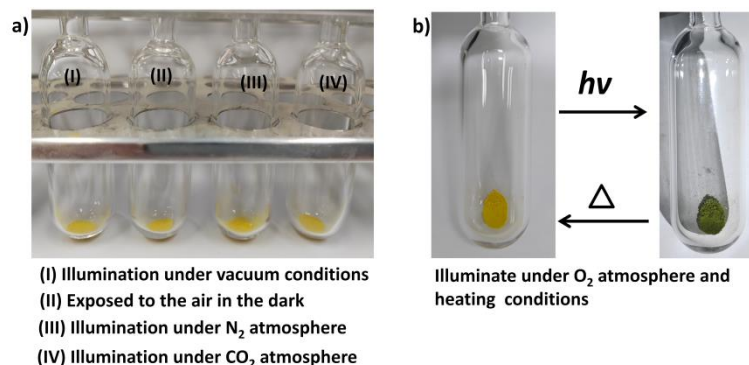
1. The experiment of exposing the COF to light in a pure oxygen environment should be done to eliminate the interference of other components in the air, such as water.

Response: This is a very important point and we are grateful for the suggestion. The photochromic transformation exists under pure oxygen and light conditions, we have provided the image of photochromism under different conditions in Supplementary Figure 6.

We have added relevant discussion on the matter in the revised manuscript.

“However, there are no photochromic features under light or air alone, and no photochromic phenomenon was observed under nitrogen or carbon dioxide atmosphere when illuminated. But under oxygen conditions, photochromism occurs when illuminated, and the original color of DBTB-DETH-COF recovery under heating conditions (Supplementary Figure 6).”

We have added relevant image in Supplementary Figure 6.



Supplementary Figure 6. The photochromic features of DBTB-DETH-COF under different conditions.

2. The XRD peaks of DBTB-DETH-COF, aside from the main peak, do not align well with the simulated PXRD pattern.

Response: We thank the reviewer for this valuable observation.

Indeed, there is a slight deviation between the experimental and simulated peaks. We have re-simulated and optimized the data to achieve more consistent results. We have substituted the original image with new simulation diagram.

We have made modifications in the revised manuscript.

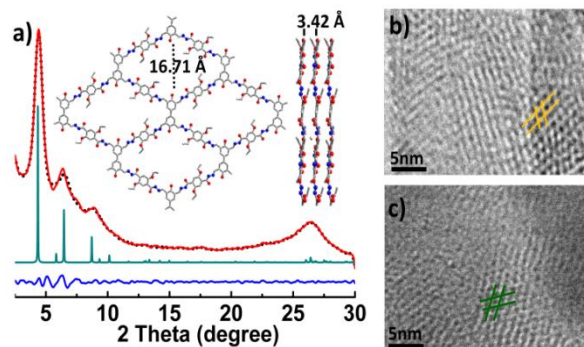


Fig. 2 The structure characterisation and analysis of **DBTB-DETH-COF**.

“To interpret the lattice information, the calculation was adopted to optimize the conformation of the 2D eclipsed (AA) stacking model (Supplementary Table 1). In contrast, the 2D staggered (AB) modes did not agree with the experimental results (Supplementary Table 2, Supplementary Figure 1c). The PXRD pattern with the P_1 space group gave the unit cell parameters of $a = b = 20.4000 \text{ \AA}$, $c = 3.4200 \text{ \AA}$, and $\alpha = \beta = 90^\circ$, $\gamma = 84.1964^\circ$. The reproducible parameters are in line with the experimentally observed pattern with a negligible difference ($R_{wp} = 2.09\%$ and $R_p = 1.56\%$).”

3. Please provide the PXRD of AP-DBTB-DETH-COF.

Response: We thank the reviewer for pointing out this issue and apologize for not describing clearly.

The PXRD pattern of DBTB-DETH-COF under light for 15 days (Supplementary Figure 2.a) is the PXRD pattern AP-DBTB-DETH-COF.

We have highlighted this part in the revised Supplementary part (Supplementary Figure 8).

“**Supplementary Figure 8**. 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.”

4. Labels “b” and “c” in Fig. 7 do not correspond to the legend below the

Figure.

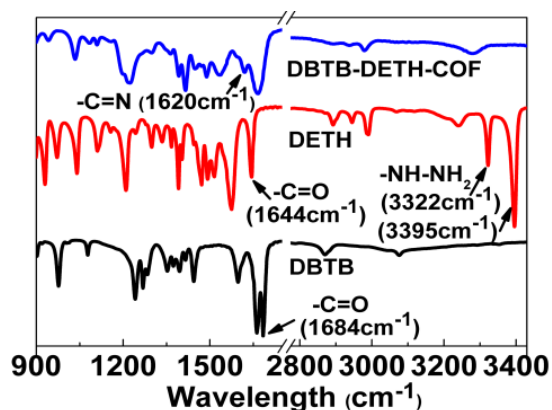
Response: We thank the reviewer for this feedback and we apologize for this oversight.

We have corrected the figure 7 in the revised manuscript.

“**Fig. 7** Transient absorption spectra of DBTB-DETH-COF. **a** DBTB-DETH-COF under N_2 atmosphere. **b** two-dimensional spectro-temporal transient absorption map showing the change in optical density (OD) in N_2 . **c** DBTB-DETH-COF under O_2 atmosphere. **d** two-dimensional spectro-temporal transient absorption map showing the change in optical density (OD) in O_2 (343 nm excitation).”

5. In line 51, the wavelength of C=N linkage is referred to 1620 cm^{-1} , but in Supplementary Figure 1a, it is referred to 1665 cm^{-1} .

Response: We thank the reviewer for this constructive feedback and we apologize for our incorrect writing. We have corrected the data in Supplementary Figure 1a.



Supplementary Figure 1. The characterization of DBTB-DETH-COF. (a) FT-IR spectra of DBTB, DETH and DBTB-DETH-COF.

Responds to the reviewer#2' s comments:

The manuscript reports a COF with photochromic property. This is a new type of materials.

Response: We appreciate the reviewer very much for the positive comments.

1. The introduction is relatively short. A slightly broader background would be instructive for the readers.

Response: We would like to thank the reviewer for this helpful insight.

We have added background of photochromic materials and highlighted this part in the revised manuscript.

“ Nowadays, a number of inorganic, organic and inorganic-organic hybrid photochromic materials have been explored ^{5, 15-17}. The common inorganic photochromic materials include polyoxometalates, transition metal oxides, metal halides, prussian blue analogs and rare earth complexes, etc. The classic organic photochromic materials contain dithienylethene, spiropyrans, diarylethenes, chromenes, fulgides, azocompounds, viologens, and so on. The inorganic-organic hybrid photochromic materials cover hybrids of metal halides, hybrids of metal cyanides, hybrids of polyoxometalates, metal chalcogenide, and metal-organic complexes, etc. The reasons of photochromism are mainly due to the change oxidation states upon irradiation, photo-induced molecular conformations isomerization, polarity, and photoinduced electron transfer ¹⁸⁻²². Design and synthesis of new stable photochromic materials featuring fast response and high contrast are still a challenging task ^{23, 24}. ”

“and heterogeneous catalysis owing to their unique features including permanent porosity, low densities, and high surface areas. These advantages enable COFs to readily adsorb guest molecules and establish interactions with them. The more important thing is COFs have relatively high chemical, light and thermal stabilities, which make them more suitable for practical applications ²⁵⁻²⁸. ”

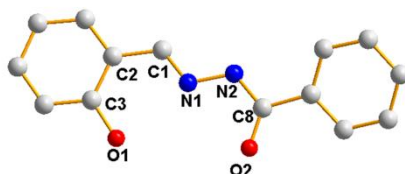
“Herein, we display a new DBTB-DETH-COF which exhibits reverse photochromism owing to photoinduced electron transfer (PET) in the presence of light and oxygen. What's more important is the coloring and fading process can be repeated at least 50 cycles without color loss.”

2. How about photochromic property of DBTB itself or a model compound? What is the advantage of COF?

Response: We thank the reviewer again for this valuable insight and advice.

The comparative experiments with DBTB, monomer model N'-(2-

Hydroxybenzylidene)benzohydrazide are made under the same conditions, the photochromic behavior cannot be observed. Perhaps due to DBTB-DETH-COF has stable pore structure that can adsorb oxygen and easily interact with oxygen. The following relevant descriptions into the experimental section of the revised supplementary information and the advantage of DBTB-DETH-COF have adjusted and highlighted in the revised manuscript.



Supplementary Figure 7. The crystal structure of monomer model N'-(2-Hydroxybenzylidene)benzohydrazide of DBTB-DETH-COF.

“As a recently emerging class of porous crystalline materials assembled through strong covalent bonds, covalent organic frameworks (COFs) have become attractive platforms for various functional materials, including gas adsorption and storage, energy storage and conversion, drug delivery, and heterogeneous catalysis owing to their unique features including permanent porosity, low densities, and high surface areas. These advantages enable COFs to readily adsorb guest molecules and establish interactions with them.”

“Herein, we display a new DBTB-DETH-COF which exhibits reverse photochromism owing to photoinduced electron transfer (PET) in the presence of light and oxygen. What’s more important is the photochromism and restoration process can be repeated at least 50 cycles without color loss.”

“In addition, the comparative experiments with DBTB and monomer model N'-(2-Hydroxybenzylidene)benzohydrazide (Supplementary Figure 7, Supplementary Table 3 and Table 4) are made under the same conditions, the photochromic behavior cannot be observed. Furthermore, the photochromic process has been further investigated by solid-state UV-vis spectroscopy.”

3. In Figure 5, there is a small peak at 533 eV for AP sample. This fitting is wrong. The FWHM of the peak should follow certain rule.

Response: We appreciate the reviewer's suggestions.

To ensure the accuracy of XPS for oxygen in **DBTB-DETH-COF**, we consulted with engineers of XPS, conducted careful inspection, and repeated testing. We have made corrections to the XPS for oxygen and found there are no changes in carbon, nitrogen, and energy spectra. Comparing the XPS spectra of oxygen in **BP-DBTB-DETH-COF** and **AP-DBTB-DETH-COF**, we found that the O1s binding energy of **BP-DBTB-DETH-COF** are located at 531.3 eV and 533.1 eV, which corresponded to C-OH/C-O-C and C=O, while after photochromism the O1s spectra can be fitted two peaks :531.5 eV and 532.2 eV, The shift of both peaks towards higher binding energy indicates a decrease in the electron cloud density.

The following relevant descriptions in the revised manuscript

“The O1s binding energy peaks of **BP-DBTB-DETH-COF** are located at 531.3 eV and 533.1 eV, which corresponded to C-OH/C-O-C and C=O, while after photochromism the O1s spectra can be fitted two peaks :531.5 eV and 532.2 eV, respectively (Fig. 5)³⁷⁻³⁹. The shift of both peaks towards higher binding energy indicates a decrease in the electron cloud density of the C-OH/C-O-C and C=O bond, which suggest that the electrons of **BP-DBTB-DETH-COF** have been transferred to O₂. This is in good agreement with the EPR experiment.”

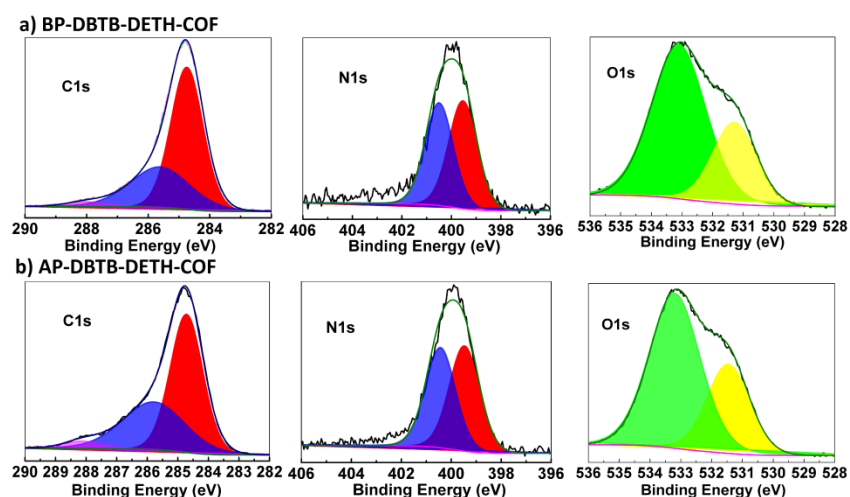


Fig. 5 XPS spectra. **a** BP-DBTB-DETH-COF. **b** AP-DBTB-DETH-COF.

4. The mechanism of photochromic is elusive. In line 83, the new adsorption bands for AP COF sample is ascribed to PET. In line 99, the photochromic is ascribed to radicals. What kind of radical? Generally, the radical is short-

lived.

Response: We thank the reviewer for pointing out this issue and apologize for not describing clearly.

The mechanisms for explaining photochromic can be mainly divided into three categories. Firstly, photoisomerization induces diarylethene, spiropyran, and azobenzene derivatives. Secondly, the change oxidation states upon irradiation, such as WO_3 , MoO_3 , V_2O_5 and TiO_2 , and so on. Thirdly, viologen and naphthalene diimide derivatives can undergo photoinduced electron transfer (PET) between the electron donor and electron acceptor to form corresponding radicals upon irradiation.

In the absence of oxygen, the phototropism cannot occur under light irradiation, indicating that **BP-DBTB-DETH-COF** interacts with oxygen and there may be electron transfer between them. EPR testing proves that oxygen produces superoxide anions and the pore structure of **BP-DBTB-DETH-COF** stabilizes superoxide anions.

In line 83, the new adsorption bands for **AP-DBTB-DETH-COF** sample is ascribed to PET have deleted and In line 99, The photochromic is ascribed to radicals have modified and rephrased this section.

“**AP-DBTB-DETH-COF** is essentially identical with **BP-DBTB-DETH-COF**, suggesting that **DBTB-DETH-COF** has strong fatigue-resistance property and no bond cleavage/formation or lattice rearrangement occurs. **DBTB-DETH-COF** did not exhibit photochromic phenomenon under illumination in the absence of oxygen, indicating that **DBTB-DETH-COF** itself does not exhibit photochromic behavior.”

“Both conditions display the maximum positive value at 575 nm, this signal can be assigned to the absorption derived from PET and the signal value in oxygen is greater than that in nitrogen, which suggesting that oxygen can promote electron transfer. No photochromism occurred under light without O_2 , indicating photochromism is not caused by electron transfer within **BP-DBTB-DETH-COF** itself, but due to photoinduced electron transfer (PET) between **DBTB-DETH-COF** and O_2 . Photochromism of **DBTB-DETH-COF** occurs under oxygen and light, the

presence of $\bullet\text{O}_2^-$ was detected through EPR, indicating that **DBTB-DETH-COF** reacted with O_2 to produce $\bullet\text{O}_2^-$, and the transfer of electrons from **BP-DBTB-DETH-COF** to O_2 was confirmed by XPS and TA. **BP-DBTB-DETH-COF** undergoes a color change to form **AP-DBTB-DETH-COF** after losing electrons, while O_2 form $\bullet\text{O}_2^-$ after gaining electrons. Additionally, the pore structure of **DBTB-DETH-COF** plays a role in stabilizes the $\bullet\text{O}_2^-$. Under heating conditions, $\bullet\text{O}_2^-$ return electrons to **AP-DBTB-DETH-COF** form O_2 and **BP-DBTB-DETH-COF**, the COF restore the original color.”

5. There are many grammatic errors and typos in the manuscript.

Response: We express thanks to the reviewer for catching this mistake and apologize for this oversight. We have corrected the mistake in the revised manuscript.

- 1) **DBTB-DETH-COF** fonts that are not bolded have already been bolded.
- 2) The O_2^- has been corrected and highlighted in yellow in EPR section.
- 3) Change “crystalline porous material” to “crystalline porous materials” in abstract section.
- 4) “The reasons of photochromism are mainly due to the change oxidation states upon irradiation, photo-induced molecular conformations isomerization, polarity, and photoinduced electron transfer” remove reason of in introduction section.
- 5) “However, there is no report the other type photochromic COF.” deleted the in introduction section.
- 6) “Herein, we display a new **DBTB-DETH-COF** which exhibits reverse photochromism owing to photoinduced electron transfer (PET) in the presence of light and oxygen.” were corrected as “Herein, we display a new **DBTB-DETH-COF** which exhibits reversible photochromism owing to photoinduced electron transfer (PET) in the presence of light and oxygen.”
- 7) “The olive sample can be decolored after being heated at 100 ° C for 5 minutes.” were corrected as “The olive sample can be decolored after being heated at 100 ° C for 5 minutes.”
- 8) “The yellow **BP-DBTB-DETH-COF** sample in different scavenger under light irradiation, the yellow sample only in benzoquinone has no color variation

(Supplementary Figure 9a).” were corrected as “The yellow BP-DBTB-DETH-COF sample in different scavenger under light irradiation, only in benzoquinone has no color variation (Supplementary Figure 9a).”.

9) “This is in good agreement with the EPR experiment. The full XPS spectra is displayed in Supplementary Figure 10a, 10b” changed to “This is in good agreement with the EPR experiment. The full XPS spectra is displayed in Supplementary Figure 10a and 10b”

10) Reference 46 has been revised to superscripted and highlighted in yellow.

11) “Supplementary Figure 3. quenching experiments. (a) The color change of BP-DBTB-DETH-COF adding different quenching agents and (b) BP-DBTB-DETH-COF adding different quenching agents.” has been changed to “Supplementary Figure 9. 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.”

12) Other errors and modification are highlighted in yellow.

Responds to reviewer #3' s comments:

In this manuscript, a reversible photochromic hydrazone-linked COF DBTB-DETH-COF was reported. It showed an interesting reversible photochromism from yellow to olive in the presence of light and air, and back to the original color upon heating. Additionally, the related reason of photochromic process was discussed by various techniques and measurements. Furthermore, it was used as anti-counterfeiting ink and optical switch. Considering that there are rarely relevant reported on COFs photochromism, this work is quite of interest and novelty. It would expand the applications of COFs. Thus, I suggest its acceptance subject to some revisions, as listed in the below:

Response: we appreciated such a positive comment very much!

1. As for the synthesis of DBTB-DETH-COF, the ultrasonic method was employed and revealed several advantages in comparison to traditional solvothermal approach. However, some control experiments should be performed to confirm the

real role of ultrasonic irradiation. Since 1 h ultrasound, the solvent mixture will be heated to a high temperature. Then, the synthesis should be performed only by heating without ultrasound. On the other hand, **DBTB-DETH-COF** sample is suggested to be prepared by solvothermal approach. And the as-synthesized sample should be compared with the sample from ultrasonic method in crystallinity, surface area, chemical stability and photochromism, in order to further confirm the advantages of ultrasonic method.

Response: We thank the reviewer for pointing out this issue.

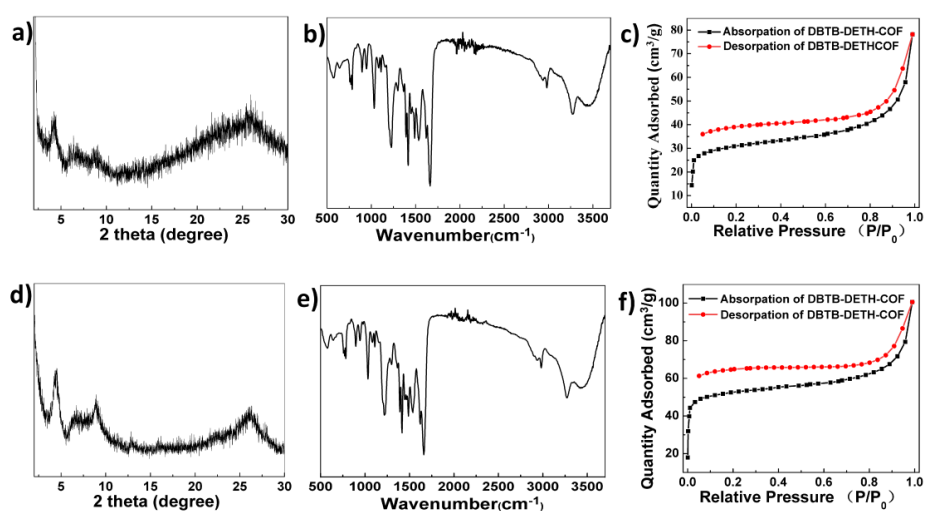
When synthesizing under ultrasound conditions, we overlooked the temperature rise, and the water temperature actually reaching 60 ° C after 1 hour. The control experiments did not obtain better crystallization of **DBTB-DETH-COF** under ultrasound at 0 ° C for 1 hour and heating at 60° C for 1 hour. The PXRD, FT-IR spectra, and BET for the control experiments have been added in the supplementary information (Supplementary Figure 2). But good crystallization can be obtained under solvothermal conditions in the dioxane/mesitylene mixture was sealed in a Pyrex tube under N₂ at 120 ° C for 3 days. The synthesis of **DBTB-DETH-COF** under solvothermal conditions is added in Supplementary Sections and **DBTB-DTPH-COF** synthesized under solvothermal conditions was characterized by PXRD, FT-IR, BET, (CP-MAS) NMR, TGA analysis (Supplementary Figure 3) and photochromism (Supplementary Figure 5). The crystallinity of **DBTB-DTPH-COF** obtained by solvothermal method is similar to that of ultrasound method, but ultrasound method takes less time and is easier to synthesize in large quantities. The stability of **DBTB-DTPH-COF** formed by the ultrasound conditions and solvothermal conditions are also similar (Supplementary Figure 4).

The relevant contents have been added in Supplementary section (Supplementary Figure 2-5)

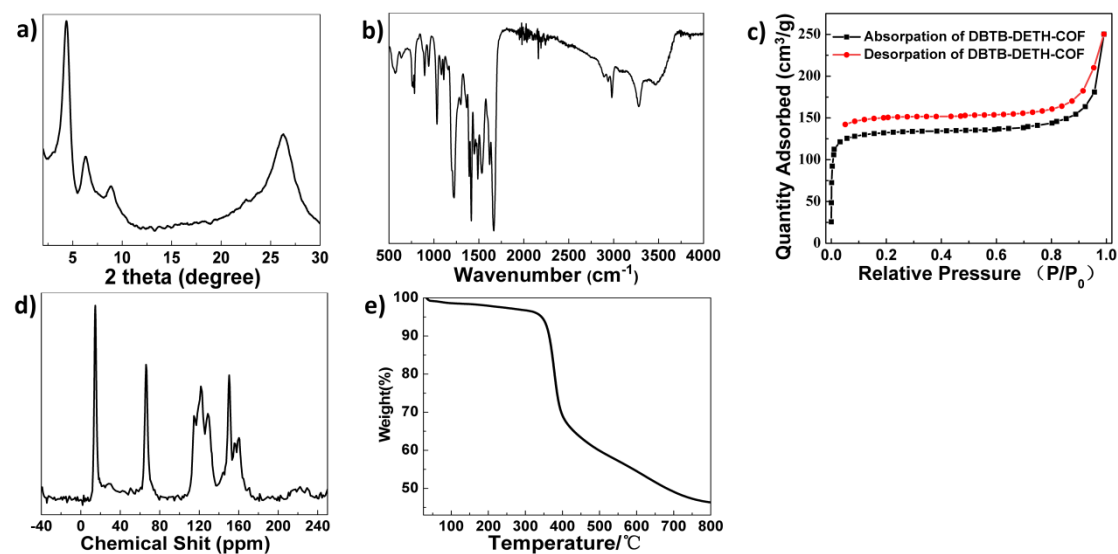
Chemical stability test of DBTB-DTPH-COF

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 H₂O solution at room temperature for 3 days, NaBH₄ (1 M) in

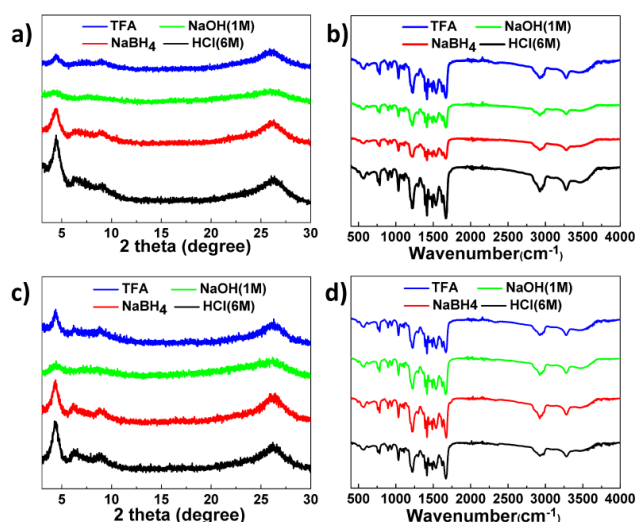
methanol at room temperature for 3 days and 0.5 mL trifluoroacetic acid (TFA) at room temperature for 3 days, The sample was washed with ethyl alcohol for 3 times, dried under vacuum at 60 °C and measured by PXRD measurements and FT-IR spectra.



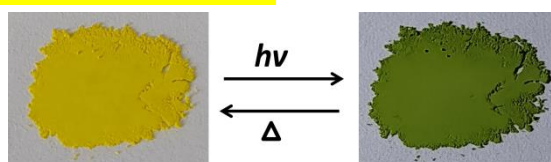
Supplementary Figure 2. a) the PXRD, b) FT-IR spectra, and c) BET of DBTB-DETH-COF synthesized under ultrasound at 0 ° C for 1 hour, and d) the PXRD, e) FT-IR spectra, f) BET of DBTB-DETH-COF synthesized under heating at 60° C for 1 hour.



Supplementary Figure 3. a) the PXRD, b) FT-IR and c) BET, d) The solid state ¹³C cross-polarization magic-angle-spinning (CP-MAS) NMR, e) TGA of DBTB-DTPH-COF synthesized under solvothermal conditions.



Supplementary Figure 4. a) the XRD patterns and b) FT-IR of DBTB-DTPH-COF synthesized under ultrasound condition in different media 3d at RT. c) the XRD 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.

The revised manuscript has been modified and adjusted.

“ More than 10g crystallinity DBTB-DETH-COF was quickly obtained within 1 hour from the condensation of 4,4'-dihydroxy-[1,1'-biphenyl]-3,3',5,5'-tetracarbaldehyde (DBTB) and 2,5-diethoxyterephthalohydrazide (DETH) under ultrasound conditions as shown in Fig. 1.”

“HR-TEM revealed that DBTB-DETH-COF has grid structure with pores of around 1.5nm (Fig. 2b), which is well consistent with its structural modeling analysis. In order to optimize the synthesis conditions of DBTB-DETH-COF, the control experiments were conducted as the water temperature was raised to 60° C under ultrasound condition. The experiments under ultrasound at 0 ° C for 1 hour and heating at 60° C for 1 hour did not obtain high crystallinity DBTB-DETH-COF (Supplementary Figure 2). But DBTB-DETH-COF with high crystallinity can be obtained under solvothermal conditions in the dioxane/mesitylene mixture was sealed in a Pyrex tube at 120 ° C for 3 days (Supplementary Figure 3). The

ultrasonic method is more efficient and time saving, more importantly, it is easier to obtain a large amount of products compared to traditional solvothermal approach. The stability of **DBTB-DTPH-COF** formed through solvothermal method and the ultrasound method are also similar (Supplementary Figure 4). It is noteworthy that **DBTB-DTPH-COF** has poor stability in NaOH solution.”

“The olive sample can be decolored after being heated at 100 ° C for 5 minutes. The **DBTB-DETH-COF** obtained under solvothermal condition exhibit the same photochromic behavior as the **DBTB-DETH-COF** obtained under ultrasound (Supplementary Figure 5).”

2. The experimental procedure for **DBTB-DETH-COF** photochromism should be added into the main article. Besides, a real time video for monitoring such photochromism from yellow to olive and back to yellow is suggested to be added as supplementary materials.

Response: We thank the reviewer for this beneficial advice.

The photochromic procedure for **DBTB-DETH-COF** has been added in the methods part. The photochromic transformation of **BP-DBTB-DETH-COF** from yellow to olive (Supplementary Movie 1) and the olive sample **AP-DBTB-DETH-COF** restored to yellow by heating (Supplementary Movie 2) have been added and uploaded.

We have added relevant discussion in methods part in the revised manuscript.

“**DBTB-DETH-COF** exhibits a promising photochromic transformation from yellow to olive upon exposure to xenon light for 5 minutes (Fig. 3, Supplementary Movie 1). The olive sample can be decolored after being heated at 100 ° C for 5 minutes (Supplementary Movie 2).”

“The photochromic procedure for **DBTB-DETH-COF** **BP-DBTB-DETH-COF** exhibits a promising photochromic transformation from yellow to olive after irradiation with visible-light under xenon lamp (300W with the intensities 2.5W cm^{-2}) for 5 minutes. And the sample **AP-DBTB-DETH-COF** is heated on heating plate at 100 ° C for 5 minutes. The olive sample restore to yellow.”

3. As for the mechanism of photochromism, authors attributed it to be caused by

superoxide radicals which formed through electron transfer induced by photoexcitation. However, this superoxide radical is not stable and can not survive for a long time. Moreover, it is not olive color. Thus, the color change of **DBTB-DETH-COF** after photochromism should be caused by the change of COF itself. Then, which part of COF? And how did it back to yellow after heating? These things are not quite clear.

Response: We appreciate the reviewer's suggestions. I am sorry that this part was not clear in the original manuscript. We have added relevant discussion in the revised manuscript.

“Both conditions display the maximum positive value at 575 nm, this signal can be assigned to the absorption derived from PET and the signal value in oxygen is greater than that in nitrogen, which suggesting that oxygen can promote electron transfer. No photochromism occurred under light without O_2 , indicating photochromism is not caused by electron transfer within **BP-DBTB-DETH-COF** itself, but due to photoinduced electron transfer (PET) between **DBTB-DETH-COF** and O_2 . Photochromism of **DBTB-DETH-COF** occurs under oxygen and light, the presence of $\bullet O_2^-$ was detected through EPR, indicating that **DBTB-DETH-COF** reacted with O_2 to produce $\bullet O_2^-$, and the transfer of electrons from **BP-DBTB-DETH-COF** to O_2 was confirmed by XPS and TA. **BP-DBTB-DETH-COF** undergoes a color change to form **AP-DBTB-DETH-COF** after losing electrons, while O_2 form $\bullet O_2^-$ after gaining electrons. Additionally, the pore structure of **DBTB-DETH-COF** plays a role in stabilizes the $\bullet O_2^-$. Under heating conditions, $\bullet O_2^-$ return electrons to **AP-DBTB-DETH-COF** form O_2 and **BP-DBTB-DETH-COF**, the COF restore the original color.”

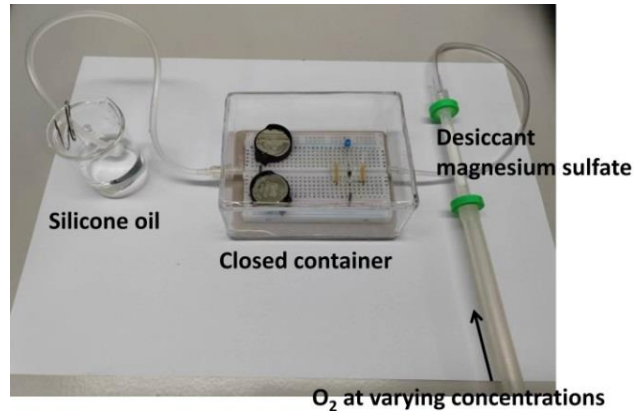
4. It is very interesting that **Graphene/DBTB-DETH-COF** composite material can be used as oxygen detecting sensor. So, can this device be used to quantitatively analyze the concentration of oxygen? Then, it would be more applicable for the practical applications.

Response: That is an excellent question, which was also of our interest.

The photochromic process of **DBTB-DETH-COF** is influenced by temperature and the amount of O_2 , In addition it is also dependent on the time of light exposure.

More importantly, the increase in brightness of the lamp is a gradual process, which is difficult to detect the concentration of oxygen. We attempted using the device to detect the concentration of O_2 . Unfortunately, results are unavailable at this point.

Therefore, this section has not been added in the manuscript.



The device to detect the concentration of O_2 .

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

I am OK with the revision and recommend the publication

Reviewer #2 (Remarks to the Author):

The reviewer is satisfactory to most of the revision. The model compound is probably too simple to represent the key feature of DBTB.

Reviewer #3 (Remarks to the Author):

Most of concerns have been properly addressed in the revision. Thus, I suggest its acceptance.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author): I am OK with the revision and recommend the publication.

Reviewer #2 (Remarks to the Author): The reviewer is satisfactory to most of the revision. The model compound is probably too simple to represent the key feature of DBTB.

Reviewer #3 (Remarks to the Author): Most of concerns have been properly addressed in the revision. Thus, I suggest its acceptance.

Point-by-point response to the referees' comments

Reviewer #1 (Remarks to the Author): I am OK with the revision and recommend the publication.

Response: Thanks to the reviewer for the highly positive remarks.

reviewer #2 (Remarks to the Author): The reviewer is satisfactory to most of the revision. The model compound is probably too simple to represent the key feature of DBTB.

Response: we thank the reviewer again for this valuable insight and advice.

The comparative experiments 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) are made under the same conditions, the photochromic behavior also not be observed. The following relevant descriptions was added in the revised manuscript and supplementary information.

we have added relevant content in the revised manuscript.

“In addition, the comparative experiments with DBTB and monomer model N'-(2-Hydroxybenzylidene)benzohydrazide (Supplementary Figure 7, Supplementary Table

3 and Table 4) and 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 7, Supplementary Figure 8) are made under the same conditions, the photochromic behavior be observed.”

we have added relevant experiment and image in Supplementary Figure 7 and

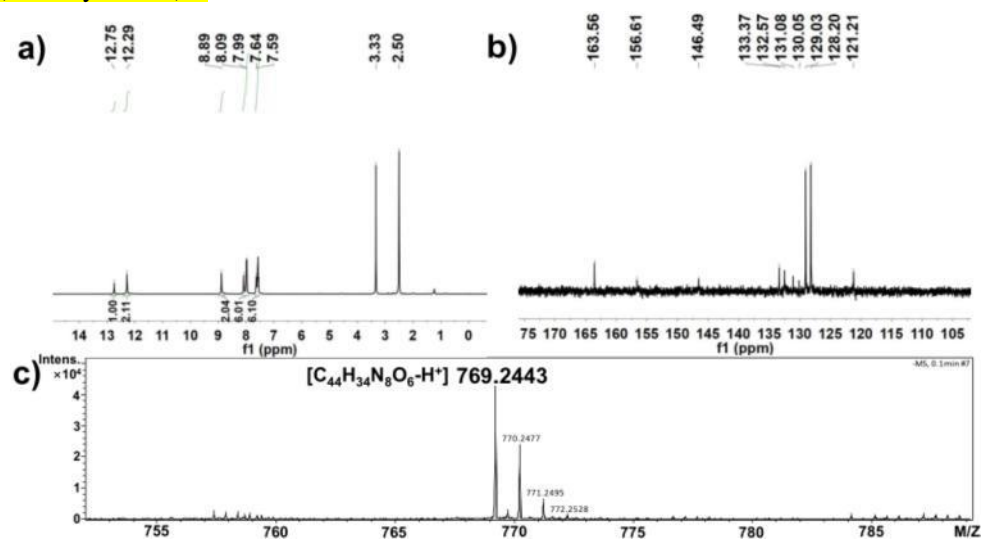
Supplementary Figure 8.

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 °C 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). ¹H NMR (400 MHz, DMSO-d₆). 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). ¹³C NMR (100 MHz, DMSO-d₆). 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 C₄₄H₃₄N₈O₆, 769.2504 ([M-H⁺]), found: m/z 769.2443.



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) ¹H NMR, b) ¹³C NMR and c) ESI-MS.

Reviewer #3 (Remarks to the Author): Most of concerns have been properly addressed in the revision. Thus, I suggest its acceptance.

Response: Thank the reviewer for the highly positive comments and the efforts in reviewing this manuscript.

Reviewer #2 (Remarks to the Author): The revision has addressed the issue and is recommended for publishing

