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Donor-acceptor modified UiO-67 type metal-organic frameworks for the enhancing photoreduction of tetracycline under visible light

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Note added after first publication:

This supplementary information file replaces that originally published on 23 November 2023. This updated file provides corrected data for Figure S2. This does not affect the results or conclusions of the work.

Content

1. Syntheses and Experimental Procedures

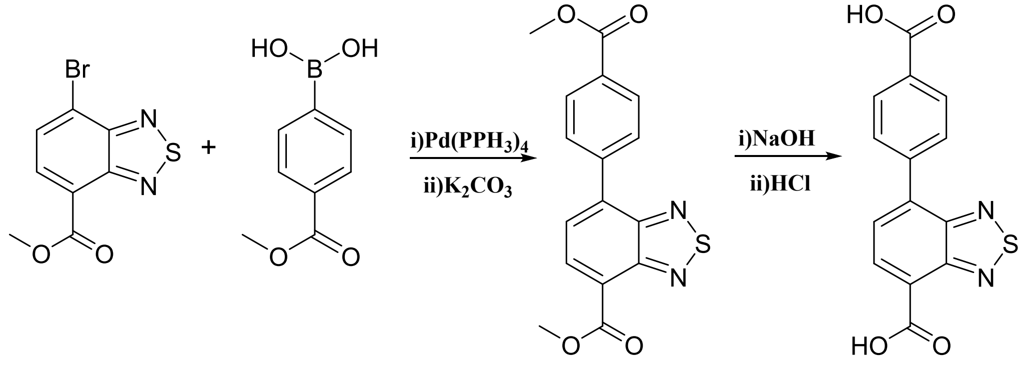
1.1 General Information

All chemicals and reagents were used from commercial sources and were not purified. Solvents for chemical synthesis were purified by distillation. All organic synthesis reactions were carried out under nitrogen. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D2 phase apparatus. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TG-7 analyzer, heated from 30 to 800 °C under nitrogen. Shimadzu UV-3101PC photometer was used for UV-vis absorption spectra. Electron paramagnetic resonance (EPR) spectroscopy was measured on EMX-nano with Xe Lamp (CEL-HXF300) as light source. Photoelectrochemical tests were performed using a computer-controlled electrochemical workstation (Chi 760E). The solid-state fluorescence emission spectra were measured on the Hitachi F7000 spectrometer.

1.2 Synthesis of ligands

Synthesis of H_2BT

Methyl 7-bromobenzo[c][1,2,5]thiadiazole-4-carboxylate (2.73 g, 10 mmol), K_2CO_3 (2.76 g, 20 mmol), $Pd(PPh_3)_4$ (0.58 g, 0.5 mmol), 4-methoxycarbonylbenzeneboronic acid (2.16 g, 12 mmol), and THF (70 ml) were mixed and refluxed for 3 days under N_2 protection. The mixture was cooled to room temperature, and THF was removed under vacuum. The residue was operated by column chromatography to obtain the yellow solid methyl 7-(4-methoxycarbonylphenyl)benzo[c][1,2,5]thiadiazole-4-carboxylate (1.64 g, 51%). The intermediate ester (1.64 g, 5 mmol), methanol (10 mL) and sodium hydroxide (50 mL, 5 mmol) were refluxed overnight. Acidification with dilute hydrochloric acid afforded 7-(4-carboxyphenyl)benzo[c][1,2,5]thiadiazole-4-carboxylic acid (1.3 g, 86%) as a yellow solid. ^1H NMR (500 MHz, DMSO-d) δ 13.28 (s, 2H), 8.41 (s, 1H), 8.40 (s, 1H), 8.13 (s, 2H), 8.04 (d, *J* = 7.39Hz, 2H).



Scheme 1. The synthesis route of H_2BT.

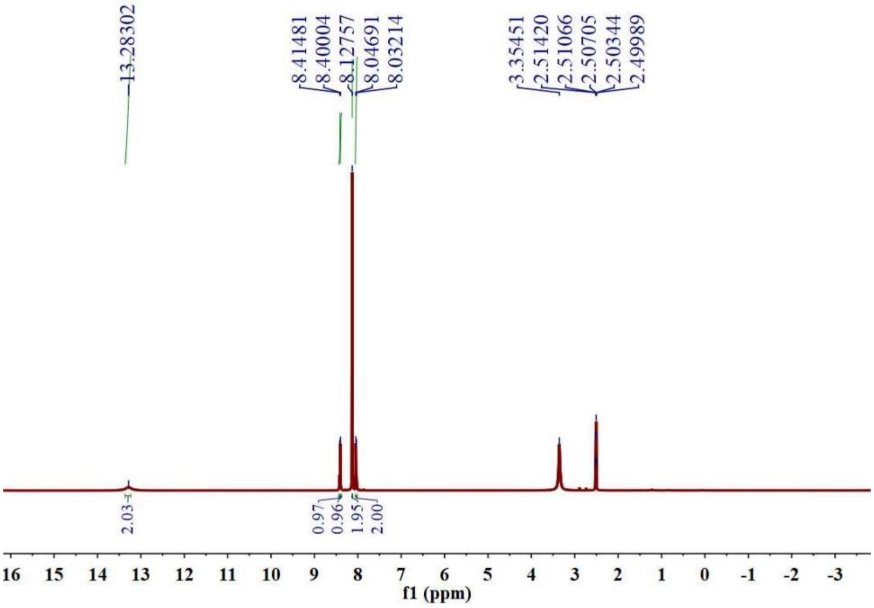
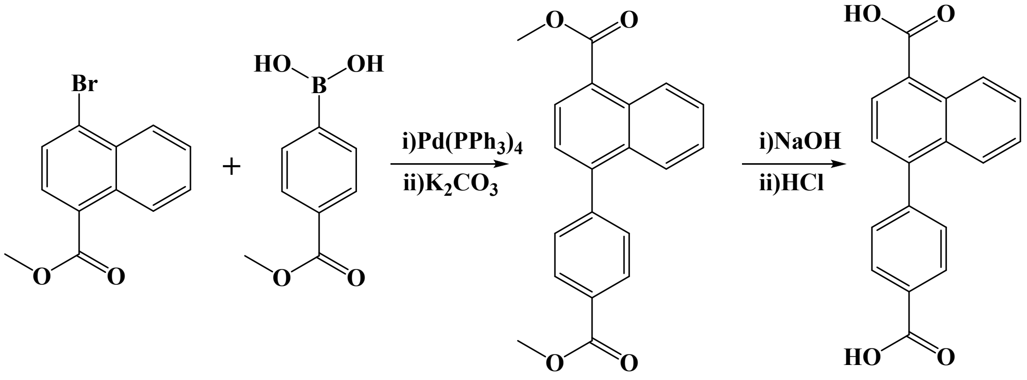


Fig. R1. ^{1}H NMR of H_2BT.

Synthesis of H_2NA

Methyl 4-bromo-1-naphthalenecarboxylate (2.65 g, 10 mmol), DMF (50 mL), K_2CO_3 (2.76 g, 20 mmol), $Pd(PPh_3)_4$ (0.58 g, 0.5 mmol), and 4-methoxycarbonylphenylboronic acid (2.16 g, 12 mmol) were mixed and stirred at reflux for 2 days under N_2 protection. After cooling, the reactants were poured into water and the mixture was extracted with $CHCl_3$ and subsequently dried with anhydrous magnesium sulfate. After the removal of $CHCl_3$, the residue was operated by column chromatography with $CHCl_3$ to give a white solid methyl 4-(4-methoxycarbonylphenyl)-1-naphthoate (2.06 g, 64%). The intermediate ester (2.06 g, 6.4 mmol), methanol (10 mL) and sodium hydroxide (30 mL, 90 mmol) were refluxed and stirred overnight. After cooling, the mixture was then acidified with dilute hydrochloric acid to give 4-(4-carboxyphenyl)-1-naphthoic acid (2.0 g, 97%) as a white solid. ^{1}H NMR (500 MHz, DMSO-d) δ 13.20 (s, 2H), 8.96 (d, $J = 8.5$ Hz, 1H), 8.24 – 8.18 (m, 1H), 8.15 – 8.07 (m, 2H), 7.82 (d, $J = 8.5$ Hz, 1H), 7.71 – 7.67 (m, 1H), 7.65 – 7.60 (m, 2H), 7.60 – 7.56 (m, 1H), 7.54 (dd, $J = 10.3$, 6.6 Hz, 1H).



Scheme 2. The synthesis route of H_2NA.

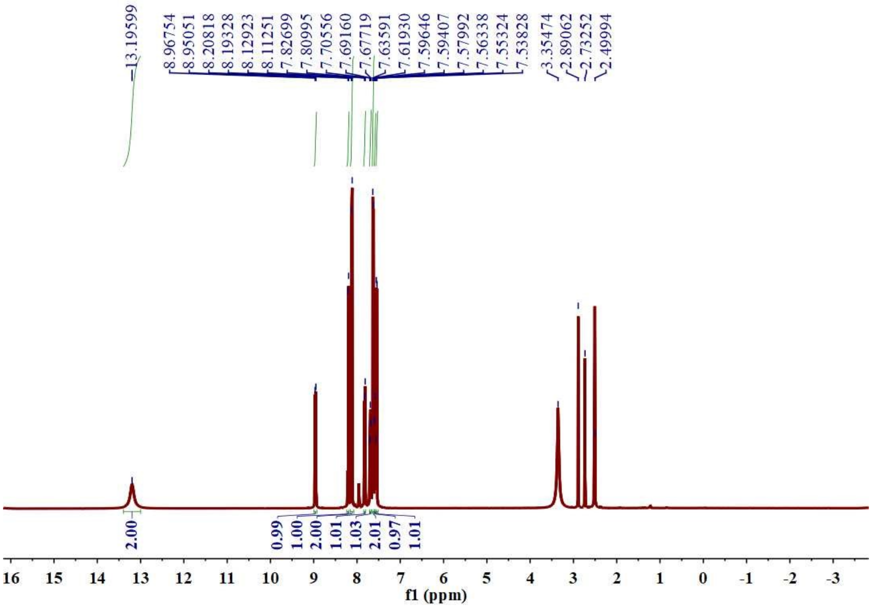
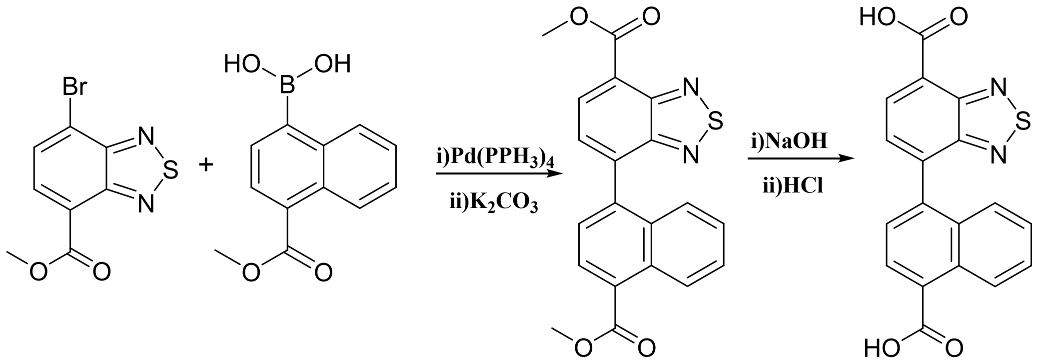


Fig. R2. ^{1}H NMR of H_2NA.

Synthesis of H_2NB

Methyl 7-bromobenzo[c][1,2,5]thiadiazole-4-carboxylate (2.73 g, 10 mmol), K_2CO_3 (2.76 g, 20 mmol), $Pd(PPh_3)_4$ (0.58 g, 0.5 mmol), (4-(methoxycarbonyl)naphthalen-1-yl)boronic acid (2.76 g, 12 mmol), THF (70 ml) were mixed and refluxed for 2 days under N_2 protection. The mixture was cooled to room temperature, and THF was removed under vacuum. The residue was operated by column chromatography with $CHCl_3$ to give a white solid methyl 7-(4-(methoxycarbonyl)naphthalen-1-yl)benzo[c][1,2,5]thiadiazole-4-carboxylate (1.38 g, 39%). The intermediate ester (1.38 g, 3.9 mmol), methanol (10 mL) and sodium hydroxide (30 mL, 90 mmol) were refluxed and stirred overnight. After cooling, it was acidified with dilute hydrochloric acid to give 4-(4-carboxyphenyl)-1-naphthoic acid (1.3 g, 95%) as a dark yellow solid. ^{1}H NMR (500 MHz, DMSO-d) δ 13.42 (s, 2H), 8.95 (d, J = 8.7 Hz, 1H), 8.47 (d, J = 7.1 Hz, 1H), 8.24 (d, J = 7.4 Hz, 1H), 7.90 (d, J = 7.1 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.52 (d, J = 8.9 Hz, 1H), 7.47 – 7.40 (m, 1H).



Scheme 3. The synthesis route of H_2NB.

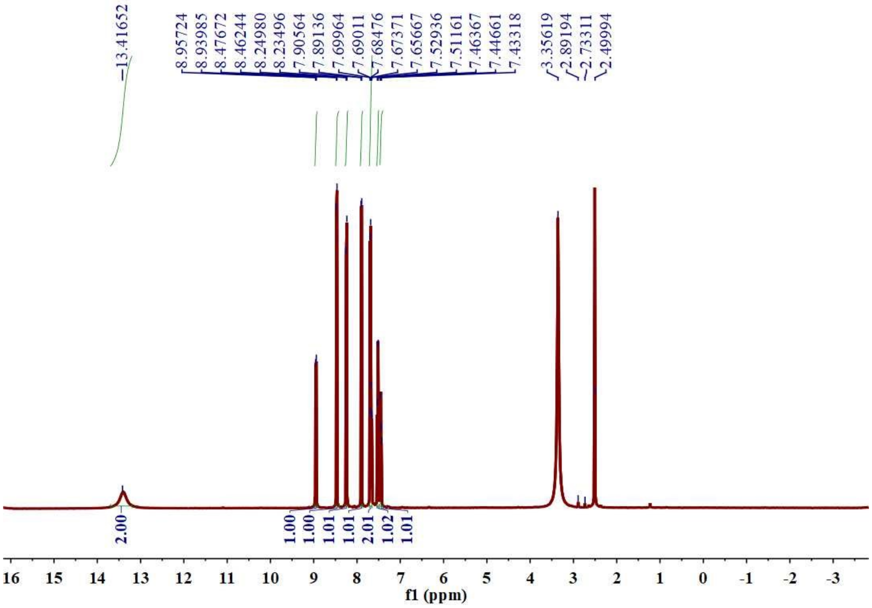


Fig. R3. ^{1}H NMR of H_2NB.

1.2 Synthesis of materials

Synthesis of UiO-67

$ZrCl_4$ (27.96 mg, 0.12 mmol), H_2bdc (16.6 mg, 0.1 mmol), DMF (5 mL) and Concentrated nitric acid (0.5 ml) were added to the reactor, sonicated for 10 min, capped and sealed, heated to 120 ℃ for 24 h. At the end of the reaction, the solid was collected by centrifugation, washed several times with DMF and methanol, and finally the solid was dried under vacuum at 50 °C for 4 hours.

Synthesis of UiO-67-NA

$ZrCl_4$ (27.96 mg, 0.12 mmol), H_2NA (29.2 mg, 0.1 mmol), DMF (7.2 mL), acetic acid (1.4 ml) and triethylamine (0.1 ml) were added to the reactor, sonicated for 10 min, capped and sealed, heated to 120 ℃ for 24 h. At the end of the reaction, the solid was collected by centrifugation, washed several times with DMF and methanol, and finally the solid was dried under vacuum at 50 °C for 4 hours.

Synthesis of UiO-67-BT

$ZrCl_4$ (27.96 mg, 0.12 mmol), H_2BT (30.00 mg, 0.1 mmol), DMF (7.2 mL) and acetic acid (0.4 ml) were added to the reactor, sonicated for 10 min, capped and sealed, heated to 120 ℃ for 24 h. At the end of the reaction, the solid was collected by centrifugation, washed several times with DMF and methanol, and finally the solid was dried under vacuum at 50 °C for 4 hours.

Synthesis of UiO-67-NB

$ZrCl_4$ (27.96 mg, 0.12 mmol), H_2NB (35.00 mg, 0.1 mmol), DMF (7.2 mL) and acetic acid (0.4 ml) were added to the reactor, sonicated for 10 min, capped and sealed, heated to 120 ℃ for 24 h. At the end of the reaction, the solid was collected by centrifugation, washed several times with DMF and methanol, and finally the solid was dried under vacuum at 50 °C for 4 hours.

2. Characterization of catalysts

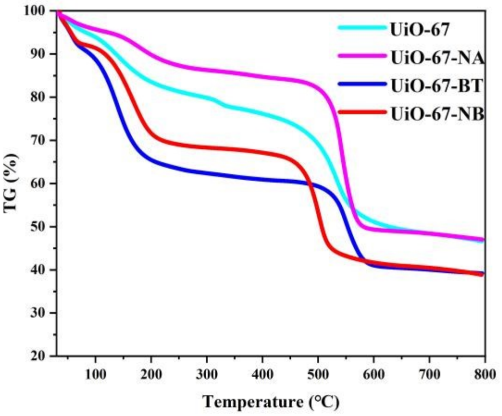


Fig. S1. TGA analyses of the four UiO-67 MOF.

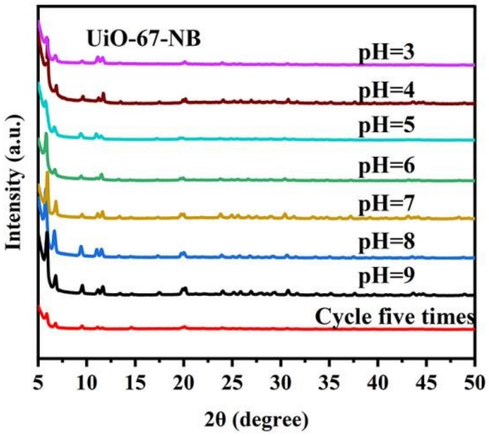


Fig. S2. PXRD analyses for UiO-67-NB MOF.

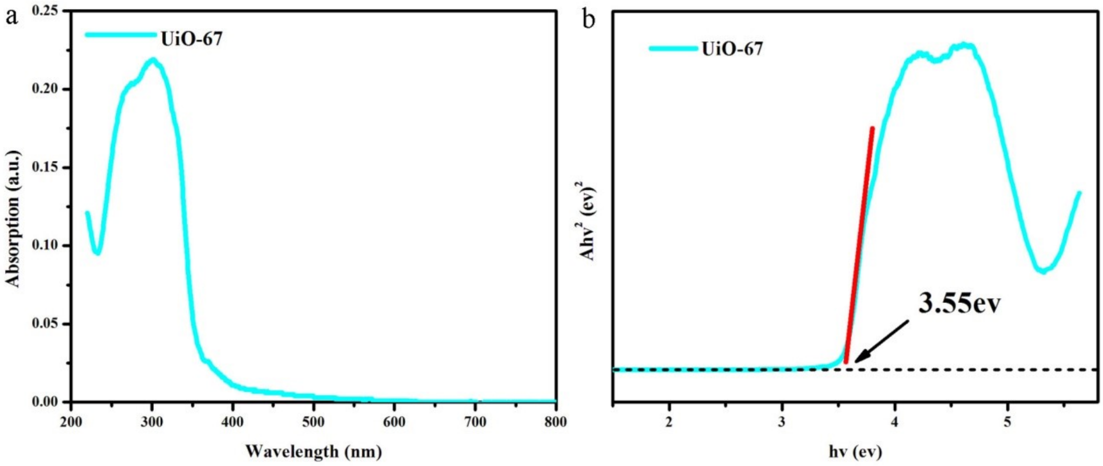


Fig. S3. Uv-vis diffuse reflectance spectra and Tauc plot for UiO-67.

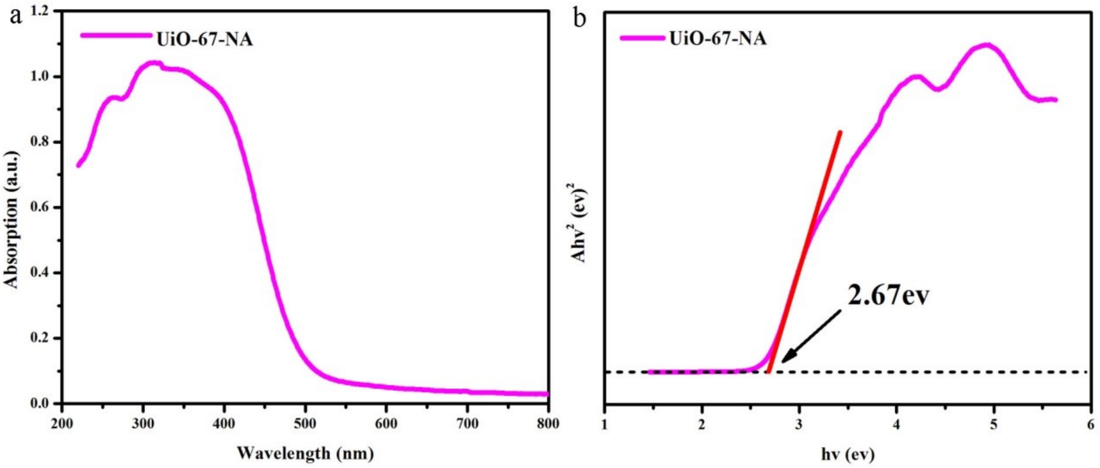


Fig. S4. Fig. S3. Uv-vis diffuse reflectance spectra and Tauc plot for UiO-67-NA.

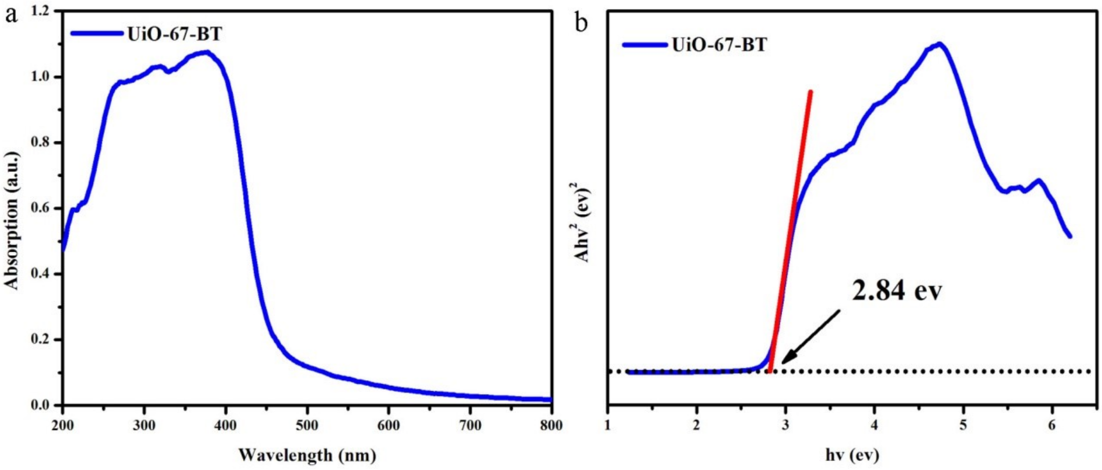


Fig. S5. Uv-vis diffuse reflectance spectra and Tauc plot for UiO-67-BT.

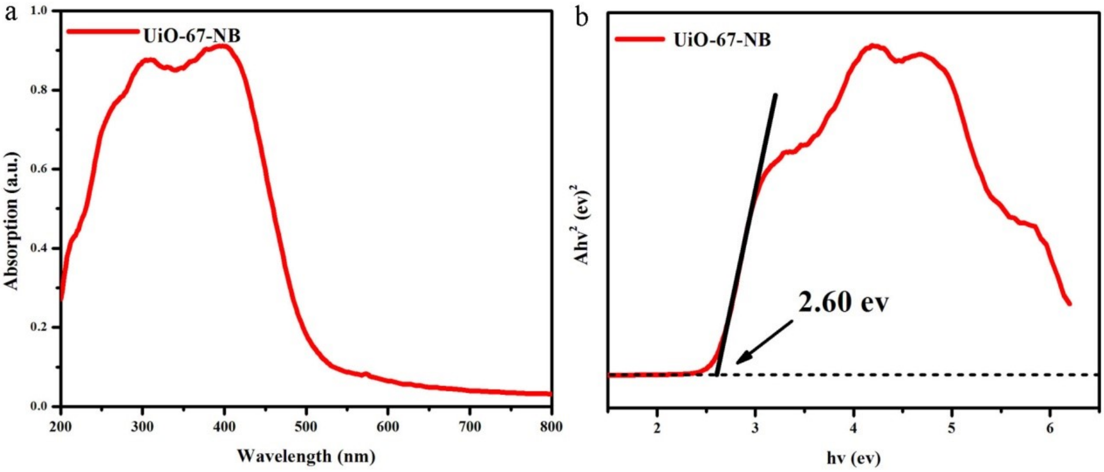


Fig. S6. Uv-vis diffuse reflectance spectra and Tauc plot for UiO-67-BT.

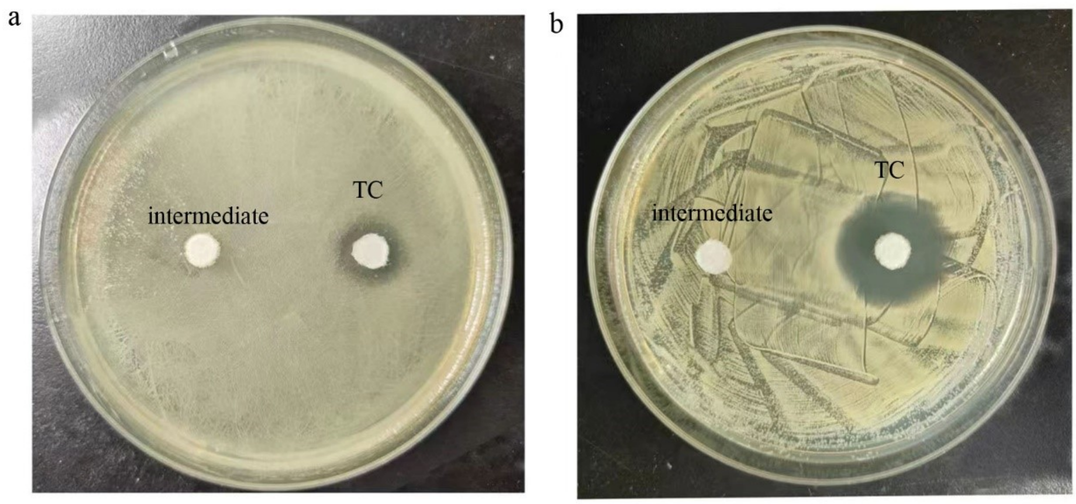


Fig. S7. The evaluation of antibacterial activities of TC and photodegradation product to Escherichia coli (a) and Staphylococcus aureus (b).

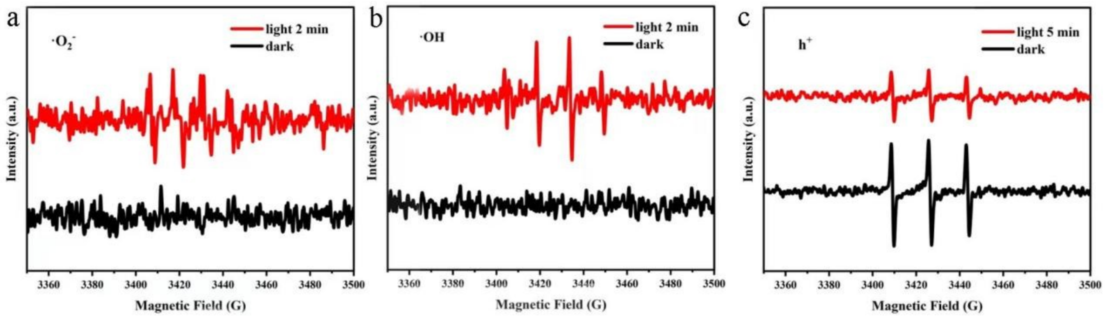


Fig. S8. ESR spectra of free radicals and holes trapped by DMPO ($\cdot O_2^-$ and $\cdot OH$) and TEMPO (h^+) in UiO-67-NA dispersion.

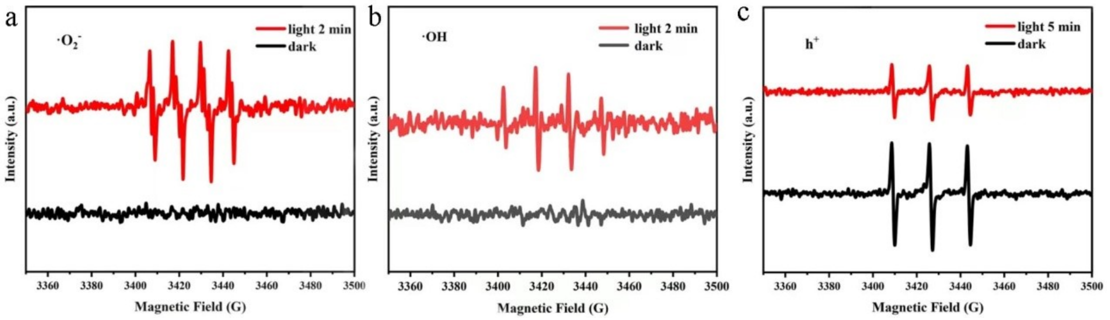


Fig. S9. ESR spectra of free radicals and holes trapped by DMPO ($\cdot O_2^-$ and $\cdot OH$) and TEMPO (h^+) in UiO-67-BT dispersion.

Table S1. Photocatalytic Activity of MOF-based materials for the reduction of TC.

Catalysts	*k* (min^{-1})	Ref.
UiO-67-NB	**0.0530**	**This work**

Ag/AgCl/BiOCl-0.5	0.0498	1
AgI/UiO-66(NH_2)	0.0360	2
Bi_2S_3/MOF-808	0.0290	3
CO/MOF	0.0283	4
DUT-5/BMO	0.0262	5
Fe-MIL-101	0.0163	6
100NU	0.0137	7
UiO-67-BT	**0.0088**	**This work**
UiO-67-NA	**0.0083**	**This work**
Fe-MIL-53	0.0023	6

3. References

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