Electronic Supplementary Information (ESI) For

AIE-active tetraphenylethene functionalized metal-organic framework for selective detection of nitroaromatic explosives and organic photocatalysis

Qiu-Yan Li,^{‡a} Zheng Ma,^{‡a} Wen-Qiang Zhang,^a Jia-Long Xu,^a Wei Wei,^a Han Lu,^a Xinsheng Zhao^b and Xiao-Jun Wang^{*a}

^aJiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry and Chemical Engineering, Jiangsu Normal University, Xuzhou 221116, P. R. China.

E-mail: xjwang@jsnu.edu.cn (X.-J. Wang)

^bSchool of Physics and Electronic Engineering, Jiangsu Normal University, Xuzhou 221116, P. R. China.

[‡]These authors contributed equally.

General method and materials

Unless specifically mentioned, all chemicals are commercially available and were used as received. NMR spectra were taken on a Bruker AV400 at room temperature. The powder X-ray diffraction (PXRD) measurements were taken on a Bruker D8 diffractometer using Cu- K_{α} radiation ($\lambda = 1.5418$ Å) at room temperature. Steady-state fluorescence measurements were carried out using a Hitachi 4500 spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a TGA-Q500 thermoanalyzer with a heating rate of 10 °C/min under nitrogen atmosphere. The solid-state emission spectra, absolute quantum yield and lifetime data were acquired on Edinburgh FLS920 instrument consisting integrating sphere. Electron paramagnetic resonance (EPR) spectra were recorded at room temperature using a Bruker ESP-300E spectrometer at 9.8 GHz, X-band, with 100 Hz field modulation. ESI-MS experiments were carried out on a ThermoFisher Q-Exactive LC-MS. Low-pressure gas sorption measurements were performed by using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with the extra-high pure gases. The as-synthesized MOF UiO-68-mtpdc/etpdc (50 mg) was immersed in CH₃OH (20 mL) for 2 day, during which time fresh CH₃OH was replaced six times. The samples were then moved into a sample cell and dried under vacuum at 80 °C and 120 °C by using the "outgasser" function of the machine for 3 h and 12 h before the measurement, respectively.

Synthesis and Characterizations



Scheme S1. The synthetic route for H₂- etpdc. Reagents and conditions: a) methyl 4-boronobenzoate, Cs₂CO₃, CsF, Pd(dppf)Cl₂, Pd(PPh₃)₄, THF/H₂O, 70 °C for 2 d; b) 4-(1,2,2-triphenylvinyl)benzaldehyde, ZrCl₄, CHCl₃, 50 °C for 2 d; c) KOH, THF, CH₃OH, 90 °C for 2 h; TFA, THF, 1 h, room temperature.

Compound 2: A mixture of Cs₂CO₃ (7.36 g, 22.5 mmol) and CsF (0.57 g, 3.75 mmol) were dissolved in water (2 mL) and added into a 250 mL round bottom flask with a magnetic stir bar. Dried and degassed THF (100 mL) was added to the reaction flask and the reaction mixture was degassed by sparging with N₂ for 2 h. Then, compound $\mathbf{1}^{[S1]}$ (2.0 g, 7.5 mmol), methyl 4-boronobenzoate (4.04 g, 22.5 mmol), Pd(dppf)Cl₂ (0.55 g, 0.75 mmol) and Pd(PPh₃)₄ (0.26 g, 0.023 mmol) were added into the mixture. The round bottom flask was vacuumed and pushed into N₂ for 5 times. The reaction was heated at 70 °C for 48 hours under an argon atmosphere. After that, the reaction mixture was cooled down to room temperature and extracted by DCM (200 mL x 2). The combined organic layer was washed with water (300 mL x 5), and dried over anhydrous Na₂SO₄ then evaporated under reduced pressure. The crude product was further purified using column chromatograph (DCM/CH₃COOC₂H₅, 100/6) to give orange solid (1.23 g, 3.27 mmol, yield: 43.6%). ¹H NMR (400 MHz, *d*₆-DMSO) δ 8.04 (d, *J* = 8.2 Hz, 4H), 7.60 (d, *J* = 8.2 Hz, 4H), 6.53 (s, 2H), 4.44 (br, 4H), 3.88 (s, 6H).

Compound 3: The compound **2** (0.30 g, 0.80 mmol) and 4-(1,2,2-triphenylvinyl)benzaldehyde^[S2] (0.30 g, 0.81 mmol) were dissolved in CHCl₃ (60 mL) and added into a 100mL round bottom flask with a magnetic stir bar. Then, $ZrCl_4$ (0.018 g, 0.08 mmol) was added into the mixture. The reaction mixture was heated at 50°C for 48h. After that, the reaction mixture was cooled down to room temperature and evaporated under reduced pressure. The crude product was further purified using

column chromatograph (DCM/petroleum ether 100/33) to give the orange solid (0.41 g, 0.57 mmol, yield: 71.5%). ¹H NMR (400 MHz, d_6 -DMSO) δ 12.70 (s, 1H), 8.37 (d, J = 7.9 Hz, 2H), 8.12-8.06 (m, 6H), 7.88 (d, J = 7.6 Hz, 2H), 7.63 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 7.4 Hz, 1H), 7.19-6.99 (m, 17H), 3.90 (d, J = 4.5 Hz, 6H).

Compound H₂-etpdc: The compound **3** (0.36 g, 0.50 mmol) was dissolved in THF (50mL) and KOH (0.28 g, 5 mmol) was dissolved in CH₃OH (5mL). Then, the two solution were added into a 100ml round bottom flask with a magnetic stir bar. The reaction mixture was heated at 90°C for 2h. After cooling down to the room temperature the reaction was separated through the suction filter to afford the yellow solid which was washed with THF (50mL x 3). Then the solid was dissolved in THF (50mL) and TFA (6mL). The reaction was stirred at room temperature for 1h. Then the solution was obtained by centrifugal to get the crude product, which was further washed by THF (50mL x 2), then washed by water (50mL x 2). At last, the product was dried to give (0.32 g, 0.47 mmol, yield: 93.2%). ¹H NMR (400 MHz, *d*₆-DMSO) δ 12.98 (s, 2H), 12.68 (s, 1H), 8.33 (d, *J* = 8.2 Hz, 2H), 8.14-8.03 (m, 6H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.22-6.96 (m, 17H).

Preparation for MOF UiO-68-mtpdc/etpdc: Organic ligands H_2 -etpdc (66 mg, 0.1 mmol), H_2 -mtpdc (33 mg, 0.1 mmol) and ZrCl₄ (51 mg, 0.22 mmol) were dissolved in DMF (75 mL), which was added into a 250 mL round bottom flask with a magnetic stir bar. Then, 3.1 mL HAc was added to the reaction flask and the reaction mixture was heated at 100 °C for 72 hours under an argon atmosphere. After cooling to room temperature, the product was separated by centrifugal to afford the white solid which was washed with DMF (100 mL x 3) and EtOH (100 mL x 3), respectively. The sample was dried in vacuum. The powder X-ray diffraction (PXRD) pattern of product was similar to the simulated pattern generated from single crystal data (Fig. S1 and S2), confirming its UiO-68 topological framework and the phase purity. The molar ratio of etpdc to mtpdc in MOF UiO-68-mtpdc/etpdc was determined to be 1:1.2. In addition, through the varying the feeding ratio of H_2 -etpdc and H_2 -mtpdc).



Scheme S2. Synthesis of 1:1 mixed strut MOF UiO-68-mtpdc/etpdc.



Fig. S1 PXRD patterns of MOF as-synthesized and activated UiO-68-mtpdc/etpdc. (MOF UiO-68-mtpdc only

contains H₂-mtpdc linker.)



Fig. S2 The zoomed-in comparison of PXRD patterns (2Theta = $3-20^{\circ}$) of as-synthesized UiO-68-mtpdc/etpdc (top) and UiO-68-mtpdc (bottom). The position of main peaks (1-10) matches very well. The variation of intensity and tiny shift may be caused by the large ligand H₂-etpdc in MOF UiO-68-mtpdc/etpdc.



Fig. S3 ¹H NMR of digested UiO-68-mtpdc/etpdc by HF in DMSO-d₆. The molar ratio of linkers H₂-etpdc and H₂-mtpdc in as-prepared MOF was calculated from the integration of He (H₂-etpdc) and H2 (H₂-mtpdc), giving the ratio of around 1:1.2, which is almost same to the initial ratio of 1:1 in preparation of MOF. The slightly higher content of H₂-mtpdc linker in MOF should be ascribed to the steric bulk of TPE moiety of H₂-etpdc linker.



Fig. S4 TGA plot of as-synthesized (left) and desolvated (right) MOF UiO-68-mtpdc/etpdc. The initial weight loss of activated sample can be attributed to the re-adsorbed water during sample weighing in air. This suggests the framework can be stable up to ~500 °C.



Fig. S5 Nitrogen sorption isotherm at 77 K (left) and BET specific surface area plot (right) of MOF

UiO-68-mtpdc/etpdc.



Fig. S6 Photographs of MOF UiO-68-mtpdc/etpdc under daylight (left) and 365 nm light (right).



Fig. S7 Emission spectra of ligand H₂-etpdc and MOF UiO-68-mtpdc/etpdc in solid state at room temperature.



Fig. S8 Photographs of ligand H₂-etpdc under daylight (left) and 365 nm light (right).

Table S1. Photophysical parameters for ligand H₂-etpdc and MOFs as well as their quenching effect coefficient (k_{sv})

	$\lambda_{em,\ max},\ nm$	Φ, %	lifetime, ns (% contribution)	$k_{\rm sv}, 10^4 {\rm M}^{-1}$
H ₂ -etpdc	518	32	τ ₁ 1.83 (48), τ ₂ 5.15 (52)	-
UiO-68-mtpdc/etpdc	490	48	τ_1 1.96 (55), τ_2 5.11 (45)	2.8 (TNP), 2.3 (DNP)
UiO-68-mtpdc/etpdc'	488	41	-	2.9 (TNP), 2.5 (DNP)
UiO-68-mtpdc/etpdc"	491	53	-	2.6 (TNP), 2.0 (DNP)

for TNP and DNP.



Fig. S9 ¹H NMR of digested UiO-68-mtpdc/etpdc' by HF in DMSO- d_6 , giving the molar ratio of linkers H₂-etpdc and H₂-mtpdc in as-prepared MOF to be 1:2.2 from the integration of He (H₂-etpdc) and H2 (H₂-mtpdc).



Fig. S10 ¹H NMR of digested UiO-68-mtpdc/etpdc" by HF in DMSO- d_6 , giving the molar ratio of linkers H₂-etpdc and H₂-mtpdc in as-prepared MOF to be 1:0.57 from the integration of He (H₂-etpdc) and H2 (H₂-mtpdc).



Fig. S11 Emission spectra of MOF UiO-68-mtpdc/etpdc dispersed in CH₃OH (0.02 mg/mL) upon incremental addition of DNP (left); and the corresponding Stern-Volmer plot of the quenching fluorescence intensity as a function of DNP concentration (right, $k_{sv} = 2.3 \times 10^4 \text{ M}^{-1}$).



Fig. S12 Emission spectra of MOF UiO-68-mtpdc/etpdc dispersed in CH₃OH (0.02 mg/mL) upon incremental addition of *p*-NP (left); and the corresponding Stern-Volmer plot of the quenching fluorescence intensity as a function of *p*-NP concentration (right, $k_{sv} = 7.2 \times 10^3 \text{ M}^{-1}$).



Fig. S13 Fluorescence quenching induced after addition of various nitroaromatic compounds (0.1 mM) to UiO-68-mtpdc/etpdc (0.02 mg/mL) in CH₃OH under a UV lamp (365 nm). From left to right: blank, 2,4,6-trinitrophenol (TNP), 2,4-dinitrophenol (DNP), *p*-nitrophenol (*p*-NP), 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), 1,3-dinitrobenzene (DNB), *o*-nitrotoluene (*o*-NT), *m*-nitrotoluene (*m*-NT), *p*-nitrotoluene (*p*-NT), nitrobenzene (NB).

Computational Details

For simplifying the computation, we only use TNP and etpdc-linker for calculation by Gaussian 09 software.^[S3] Density functional theory (DFT) calculations were performed by using the B3LYP functional with the 3-21G basis set. Four processing cores and 8 GB physical memory (Computing center, Department of Chemistry, Beijing Normal University) were used for the optimization. Frequencies were also calculated at the same level of theory to ensure that each stationary point corresponded to a minimum on the potential energy surface.



Fig. S14 The optimized complex structure between TNP and etpdc-linker. Several important parameters of the energy-minimized structure are listed below (*d*: distance; θ : bond angle): $d(O_{16}-H_{19}) = 1.58$ Å, $d(H_{19}-N_{38}) = 1.07$ Å, $d(H_{79}-N_{39}) = 1.01$ Å, $d(O_{16}-N_{38}) = 2.59$ Å, $\theta(O_{16}-H_{19}-N_{38}) = 156^{\circ}$. Oxygen, nitrogen, carbon and hydrogen are red, blue, gray and white, respectively.

General procedure for Aerobic CDC reactions of tetrahydroisoquinolines 1 with indoles 2 catalyzed by UiO-68-mtpdc/etpdc: The weighed photocatalyst UiO-68-mtpdc/etpdc (2 mg), 1 (0.1 mmol) and 2 (0.3mmol) were added into 2 mL CH₃OH. The reaction mixture with stirring was irradiated by blue LEDs for 12 hours under air at room temperature. ¹H NMR spectroscopy was employed to determine the yield; and ¹H NMR spectra of products **3** are in agreement with reported literature.^[S4] The catalyst for cyclic reaction was recycled by centrifugation at 10 000 rpm and washed by fresh CH₃OH two times.

Table S2 Screening of the model CDC reaction conditions^a

Ĺ		JiO-68-mtpdc/etpd blue LEDs, air		$\mathbf{\hat{b}}$
	1a 2a		3 a	
Entry	Conditions	Solvent	Time (h)	Yield $(\%)^b$
1	UiO-68-mtpdc/etpdc, 1 mg	CH ₃ OH	8	41
2	UiO-68-mtpdc/etpdc, 1 mg	CH ₃ OH	12	68
3	UiO-68-mtpdc/etpdc, 2 mg	CH ₃ OH	8	72
4	UiO-68-mtpdc/etpdc, 2 mg	CH ₃ OH	12	93
5	UiO-68-mtpdc/etpdc', 2mg	CH ₃ OH	12	79
6	UiO-68-mtpdc/etpdc", 2mg	CH ₃ OH	7	92
7	UiO-68-mtpdc/etpdc, 2 mg	CH ₃ CN	12	87
8	UiO-68-mtpdc/etpdc, 2 mg	DMF	12	83
9	No catalyst	CH ₃ OH	12	trace
10	In dark	CH ₃ OH	12	trace
11	In N ₂ atmosphere	CH ₃ OH	12	trace
12	In O ₂ atmosphere	CH ₃ OH	7	90
13 ^c	UiO-68-mtpdc, 2 mg	CH ₃ OH	12	trace
14^d	UiO-68-mtpdc/etpdc, 2 mg	CH ₃ OH	-	61

^{*a*}Reaction conditions: **1a** (0.1 mmol) and **2a** (0.3 mmol), blue LEDs ($\lambda_{max} = 450$ nm), solvent (2 mL). The reaction with stirring was conducted in air at room temperature. ^{*b*}Determined by ¹H NMR. ^{*c*}MOF UiO-68-mtpdc only contains ligand H₂-mtpdc.^[S1] ^{*d*}After 5 h reaction the MOF was filtered out (yield: 58%) and the filtrate went on for another 8 hours.



Table S3 The aerobic CDC reactions of tetrahydroisoquinolines 1 with indoles 2 photocatalyzed by

UiO-68-mtpdc/etpdc^{*a*}

^{*a*}Reaction conditions: **1** (0.1 mmol), **2** (0.3 mmol) and UiO-68-mtpdc/etpdc (2 mg) in CH₃OH (2 mL) under air at room temperature with 12 h blue LEDs ($\lambda_{max} = 450$ nm) irradiation. Yields were determined by ¹H NMR.



Table S4 The aerobic CDC reactions of tetrahydroisoquinolines 1 with nitroalkanes 4 photocatalyzed by

UiO-68-mtpdc/etpdc^{*a*}

^{*a*}Reaction conditions: **1** (0.1 mmol) and **4** (1 mL), blue LEDs ($\lambda_{max} = 450$ nm). The reaction with stirring was conducted in air at room temperature. Yields were determined by ¹H NMR.



Fig. S15 Recycling experiments of UiO-68-mtpdc/etpdc for the reaction of N-phenyltetrahydroisoquinoline and

indole.



Fig. S16 PXRD patterns of MOF UiO-68-mtpdc/etpdc after photocatalysis.







Scheme S3 Proposed mechanism for the photocatalytic aerobic CDC reaction of *N*-phenyltetrahydroisoquinoline and indole by MOF UiO-68-mtpdc/etpdc (photocatalyst, PC). ESI-MS was used to capture the intermediate of imine cation and peroxide species. Also, the main product and by-product were observed in ESI-MS spectra.







Fig. S19 ESI-MS of by-product amide.



Fig. S20 ESI-MS of intermediate imine cation 1a⁺.



Fig. S21 ESI-MS of intermediate peroxide.



Fig. S22 ¹H NMR of compound **2** in d_6 -DMSO



Fig. S23 ¹H NMR of compound **3** in d_6 -DMSO



Fig. S24 ¹H NMR of linker H_2 -etpdc in d_6 -DMSO

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