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Supporting Information

Construction of core-shell MOF@COF hybrids with Z scheme heterojunction for efficient visible light photocatalysis

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1. Apparent quantum efficiency (AQE) for the formation of *N*-benzylidenebenzylamine over **NH_2-UiO-66@TpBD-COF(21.9)**.

AQE at a variety of monochromatic visible light (400, 450, 550 or 650 nm) was obtained according to the yield of *N*-benzylidenebenzylamine over **NH_2-UiO-66@TpBD-COF(21.9)** in 1 h. The equation was as follow [1]:

$$AQE = \frac{n \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

Where n is the number of reaction electron (2 for benzylamine oxidation); M is the molar amounts of *N*-benzylidenebenzylamine formed; N_A is the avogadro constant (6.022×10^{23}); h is the Planck constant (6.626×10^{-34} J·s); c is the speed of light (3.0×10^{8} m/s); S is the irradiation area (6.25 cm^2); P is the incident light intensity at certain wavelength (10.6, 27.3, 4432.6 and 239 mW/cm^2 for 400, 450, 550 and 650 nm, respectively); t is the irradiation time (3600 s); λ is the monochromatic light wavelength (400, 450, 550 and 650 nm). As expected, the change trend in AQE was consistent with that of light absorption strength of the **NH_2-UiO-66@TpBD-COF(21.9)** (Table S1 and Fig. S1). The highest AQE reached to 10.0%, which was observed at 400 nm of monochromatic light irradiation.

Table S1. Calculated AQE of **NH_2-UiO-66@TpBD-COF(21.9)** at different wavelength

λ (nm)	Yield of product (μmol)	P (mW/cm^2)	AQE (%)
400	40	10.6	10.00
450	46	27.3	3.98
550	58	140.1	0.80
650	30	239.3	0.21

P: incident light intensity at certain wavelength

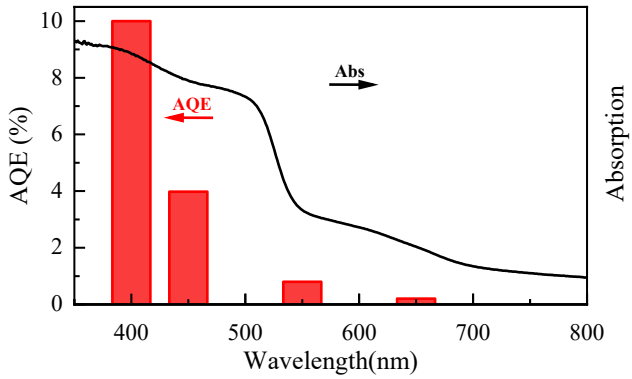

Fig. S1. The apparent quantum efficiency (AQE) for each wavelength of **NH_2-UiO-66@TpBD-COF(21.9).**

2. Determination of formed superoxide radical ($•O_2^-$), H_2O_2, and benzaldehyde during reaction.

2.1 Detection of superoxide radical ($•O_2^-$).

1,4-Bis(dimethylamino)benzene can be readily oxidized with molecular oxygen to form corresponding radical anion, accompanied by the reduction of oxygen to generate superoxide radical ($•O_2^-$). Thus, it was used as the detector of superoxide radical ($•O_2^-$).

The **NH_2-UiO-66@TpBD-COF(21.9)** (10 mg) was ultrasonically dispersed in acetonitrile (2.5 mL) in a quartz glass vial. Benzylamine (0.2 mmol, 0.022 mL) and 1,4-bis(dimethylamino)benzene (0.048 mmol, 0.008 g) were added. The mixture was stirred for 30 min in dark to achieve the adsorption-desorption equilibrium of substrate. Afterward, a 35 w halogen lamp was illuminated from the reactor top to the reaction solution under magnetic stirring. The distance between lamp and reaction solution was approximately 7 cm. The reaction was performed at room temperature under ambient air. Aliquots at an interval of 1.0 h were drawn

from the reaction mixture to determine by UV-vis spectrophotometry. Obviously, as the reaction proceeds, an absorption peak (at 553 nm) ascribed to 1,4-bis(dimethylamino)benzene radical anion appears and gradually increases in UV-vis spectra of reaction mixture. It indicated the progressive oxidization of 1,4-bis(dimethylamino)benzene to corresponding radical anion, which was accompanied by the reduction of oxygen by photo-induced electron to generate superoxide radical ($\cdot O_2^-$) (inset in Fig. S2-A) [2]. Notably, the peak didn't appear when catalyst is absence in the reaction. The results confirmed the ability of **NH_2-UiO-66@TpBD-COF(x)** to mediate the electron transfer to oxygen to generate superoxide radical ($\cdot O_2^-$).

2.2 Detection of H_2O_2.

N,N-Diethyl-1,4-phenylenediamine (DPD) was added to the reaction mixture to detect the generated H_2O_2, as DPD can be readily oxidized into DPD radical cation in the presence of H_2O_2.

The **NH_2-UiO-66@TpBD-COF(21.9)** (10 mg) was ultrasonically dispersed in acetonitrile (2.5 mL) in a quartz glass vial. Benzylamine (0.2 mmol, 0.022 mL) and N,N-diethyl-1,4-phenylenediamine (DPD, 0.06 mmol, 0.01 mL) were added. The mixture was stirred for 30 min in dark to achieve the adsorption-desorption equilibrium of substrate. Afterward, a 35W halogen lamp was used as a light source and illuminated from the reactor top to the reaction solution under magnetic stirring. The distance between lamp and reaction solution was approximately 7 cm. The reaction was performed at room temperature the ambient air. Aliquots at an interval of 1.0 h were drawn from the reaction mixture to determine by UV-vis spectrophotometry. As shown in UV-vis absorption spectra in Fig. S2-B, with the addition of DPD in reaction mixture, new absorption peaks appears at 484 and 553 nm, which is ascribed to DPD radical cation. While, they didn't appear when **NH_2-UiO-66@TpBD-COF(21.9)** is absence in the reaction. It suggests the

generation of H_2O_2 in the photoredox aerobic oxidation [3].

2.3 Detection of benzaldehyde.

The **NH_2-UiO-66@TpBD-COF(21.9)** (10 mg) was ultrasonically dispersed in acetonitrile (2.5 mL). Benzylamine (0.2 mmol, 0.022 mL) was then added. The mixture was stirred for 30 min in dark to achieve the adsorption-desorption equilibrium of substrate. Afterward, a 35 w halogen lamp was used as a light source and illuminated from the reactor top to the reaction solution under magnetic stirring. The distance between lamp and reaction solution was approximately 7 cm. The reaction was performed at room temperature the ambient air. When the reaction was performed for 2 h, the reaction mixture was characterized by ^{1}H NMR spectrum. As shown in ^{1}H NMR spectrum in Fig. S2-C, an aldehyde group-associated proton signals is obvious at the positions of 10.05 ppm. It provided the convincing evidence for the formation of benzaldehyde as a reaction intermediate.

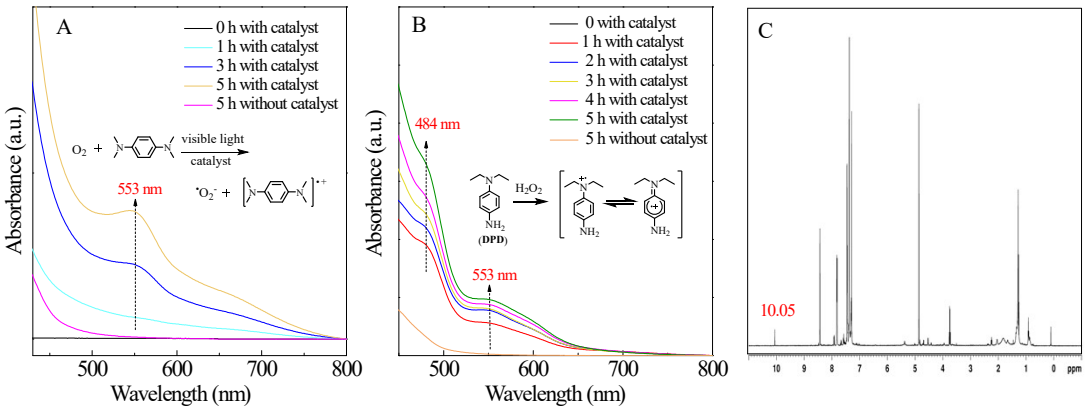

Fig. S2. (A) UV-vis spectra of 1,4-bis(dimethylamino)benzene radical anion generated by catalyst in the presence of visible light and oxygen, (B) UV-vis spectra of reaction mixture (benzylamine oxidation) with or without catalyst after adding DPD, (C) ^{1}H NMR spectrum of the reaction mixture when the reaction was performed for 2 h. (catalyst: **NH_2-UiO-66@TpBD-COF(21.9)**).

3. Identification of the obtained imines

*N-Benzylidine-p-benzylamine (**1**)*: Crude product **1** was purified by chromatography on silica gel (petroleum ether/ ethyl acetate, 18: 1). Depurated product **1** was identified by ^{1}H NMR spectrum (see Fig. S3). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.43 (s, 1 H, *H*-C=N), 7.82-7.80 (m, 2 H, Ph-*H*), 7.45-7.36 (m, 8 H, Ph-*H*), 4.86 (s, 2 H, -CH_2-).

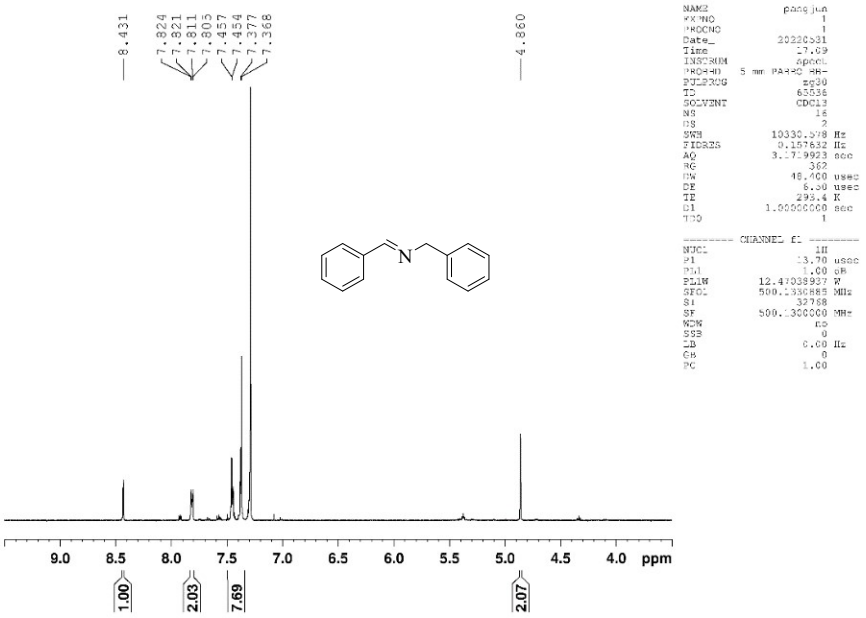

Fig. S3. ^{1}H NMR spectrum of product **1**

*N-(4-Chlorobenzylidine)-p-Chlorobenzylamine (**2**)*: Crude product **2** was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 15: 1). Depurated product **2** was identified by ^{1}H NMR spectrum (see Fig. S4). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.37 (s, 1 H, *H*-C=N), 7.74-7.73 (d, 2 H, Ph-*H*), 7.43-7.41 (d, 2 H, Ph-*H*), 7.35-7.30 (m, 4 H, Ph-*H*), 4.79 (s, 2 H, -CH_2-).

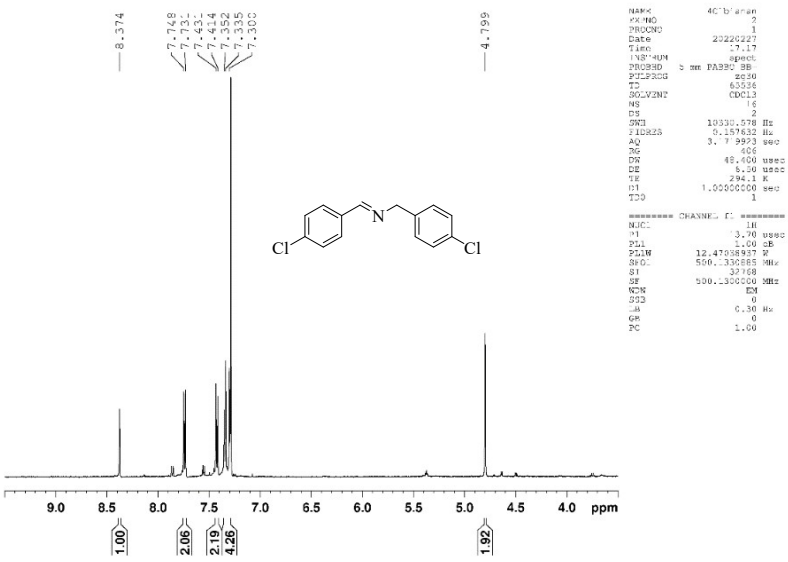

Fig. S4. ^{1}H NMR spectrum of product **2**

N-(4-Fluorobenzylidine)-p-fluorobenzylamine (3): Crude product **3** was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 15: 1). Depurated product **3** was identified by ^{1}H NMR spectrum (see Fig. S5). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.38 (s, 1 H, *H*-C=N), 8.00-7.79 (d, 2 H, Ph-*H*), 7.33-7.32 (d, 2 H, Ph-*H*), 7.14-7.05 (m, 4 H, Ph-*H*), 4.79 (s, 2 H, -CH_2-).

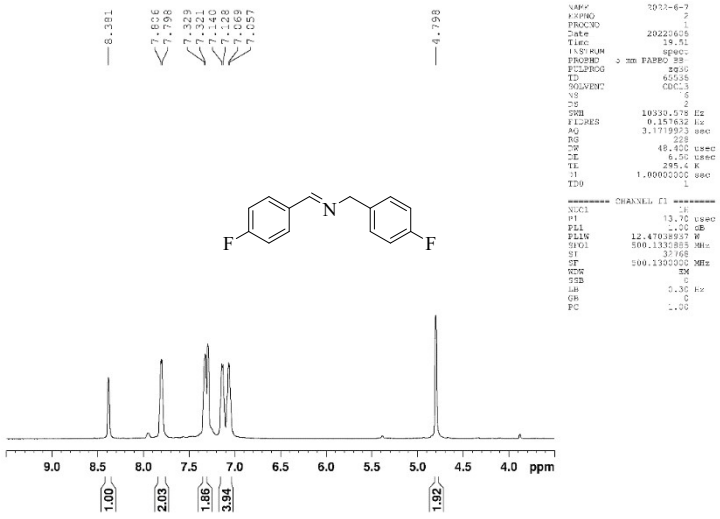

Fig. S5. ^{1}H NMR spectrum of product **3**

*N-(2-fluorobenzylidine)-o-fluorobenzylamine (**4**)*: Crude product **4** was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 16: 1). Depurated product **4** was identified by ^{1}H NMR spectrum (see Fig. S6). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.76 (s, 1 H, *H*-C=N), 8.08-8.05 (m, 1 H, Ph-*H*), 7.46-7.45 (m, 2 H, Ph-*H*), 7.32-7.31 (t, 1 H, Ph-*H*), 7.22-7.07 (m, 4 H, Ph-*H*), 4.91 (s, 2 H, -CH_2-).

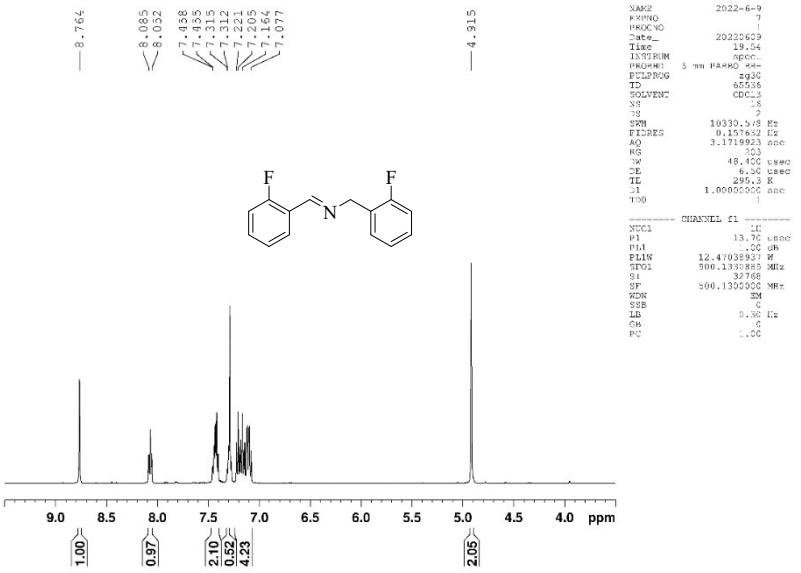

Fig. S6. ^{1}H NMR spectrum of product **4**

*N-(4-(tert-Butyl)benzylidine)-p-(tert-butyl)benzylamine (**5**)*: Crude product **5** was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 15: 1). Depurated product **2** was identified by ^{1}H NMR spectrum (see Fig. S7). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.39 (s, 1 H, *H*-C=N), 7.75-7.73 (d, 2 H, Ph-*H*), 7.4-7.45 (d, 2 H, Ph-*H*), 7.39-7.29 (m, 4 H, Ph-*H*), 4.81 (s, 2 H, -CH_2-), 1.36-1.34 (d, 18 H, -C(CH_3)$_3$).

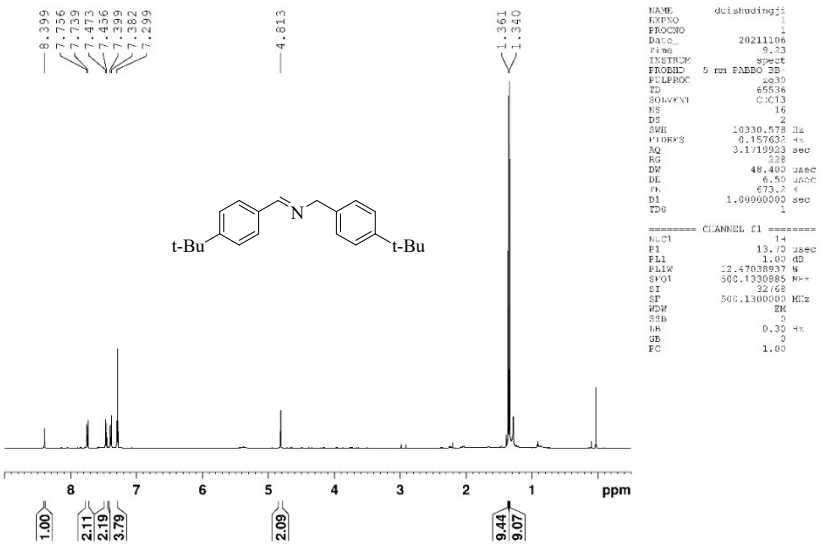

Fig. S7. ^{1}H NMR spectrum of product **5**

*1-(Thiophen-2-yl)-N-(thiophen-2-ylmethyl)methanimine (**6**)*: Crude product **6** was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 16: 1). Depurated product **6** was identified by ^{1}H NMR spectrum (see Fig. S8). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.44 (s, 1 H, *H*-C=N), 7.45-7.44 (d, 1 H, -S-C*H*=), 7.36-7.35 (d, 1 H, -S-C*H*=), 7.26 (s, 1 H, -S-CH=C*H*-), 7.11-7.09 (t, 1 H, -S-CH=C*H*-), 7.02-7.00 (m, 2 H, -S-C(C=N)=C*H*-), 4.97 (s, 2 H, -CH_2-).

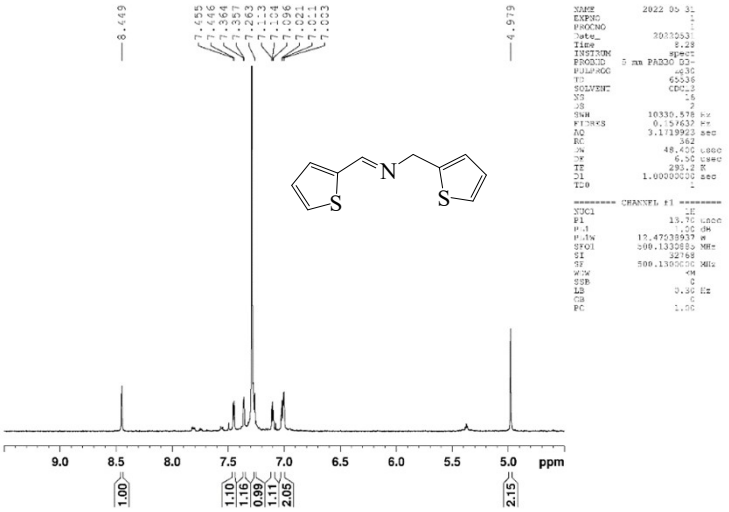

Fig. S8. ^{1}H NMR spectrum of product **6**

1-(Furan-2-yl)-N-(furan-2-ylmethyl)methanimine (7): Crude product **7** was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 20: 1). Depurated product **7** was identified by ^{1}H NMR spectrum (see Fig. S9). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.14 (s, 1 H, *H*-C=N), 7.54 (s, 1 H, -O-C*H*=), 7.41-7.40 (d, 1 H, -O-C*H*=), 6.82-6.81 (d, 1H, -O-CH=C*H*-), 6.51-6.50 (t, 1 H, --O-CH=C*H*-), 6.37-6.36 (t, 2 H, -O-C(C=N)=C*H*-), 4.78 (s, 2 H, -CH_2-).

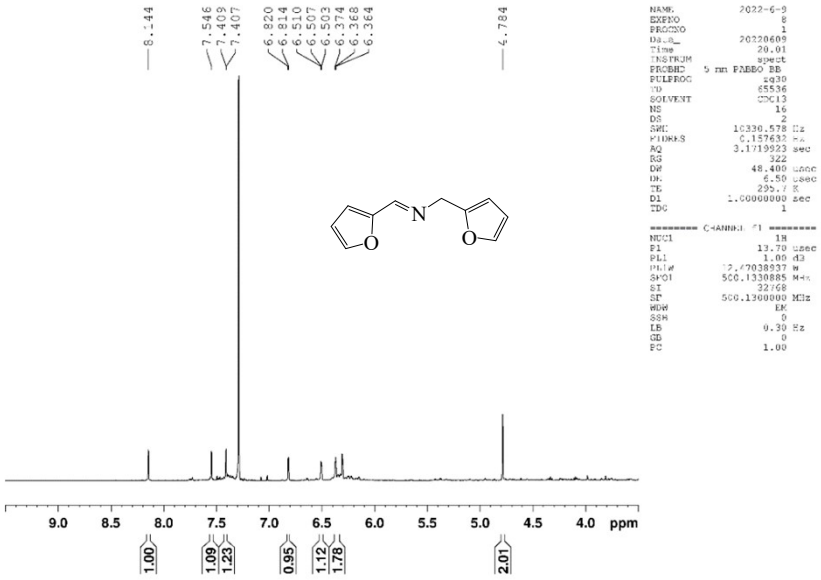

Fig. S9. ^{1}H NMR spectrum of product **7**

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