Supporting Information

Donor-acceptor covalent organic framework promotes visible light-induced oxidative coupling of amines to imines in air

Jingwen Feng #, Jie Cheng #, Jun Pang, Mingqiang Tang, Zewei Liu, Chunying Rong, and Rong Tan*

National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources; Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education); Key Laboratory of the Assembly and Application of Organic Functional Molecules of Hunan Province, College of Chemistry & Chemical Engineering, Hunan Normal University, No.36, South Lushan Road, Changsha, Hunan 410081 (P. R. China).

*Corresponding author. Email: yiyangtanrong@126.com.

# These authors should be considered as co-first authors since they contributed equally to this work.

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1. Nitrogen adsorption-desorption of the obtained COFs

Nitrogen adsorption-desorption was used to analyze the porosity of the obtained COFs, as shown in Figure S1. Both TpTt-COF and TfTa-COF showed a combined type-I/IV isotherm with type H3 hysteresis loop (Figure S1-A), which suggests the coexistence of micropores and mesopores in the hybrid materials [1]. The hierarchical porous structure is authenticated by the corresponding pore size distribution. Clearly, they show the micropores at around 1.41 nm, as well as a continuous pore diameter distribution in the range greater than 4.0 nm (Figure S1-B). We deduce that the micropore of 1.41 nm should originate from the inherent pores of TpTt-COF and TfTa-COF, while the mesopores with the size greater than 4.0 nm may be arise from the layer stacking of 2D COF sheets. The high porosity should increase the accessibility of active sites, and especially, enable rapid diffusion of charges to surface, which are desirable for the visible light-driven chemical transformation.

Figure S1. Nitrogen adsorption-desorption isotherm (A) and the corresponding pore size distribution plots (B) of TpTt-COF (a) and TfTa-COF (b)
2. Apparent quantum efficiency (AQE) for the formation of \(N\)-benzylidenebenzylamine over TpTt-COF

A commercial photo-reactor using xenon lamp as an external illumination was used to examine the apparent quantum efficiency (AQE). Monochromatic visible light at 450 nm was obtained by attaching bandpass filters to the xenon lamp and used as an external illumination. After external illumination for 30 min with xenon lamp (300 W lamp power), 47% yield of \(N\)-benzylidenebenzylamine selectivity over TpTt-COF were obtained on this photo-reactor. The AQE value was calculated using the equation [2]:

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

Where \(n\) is the number of reaction electron (2 for benzylamine oxidation); \(M\) is the molar amounts of \(N\)-benzylidenebenzylamine formed (9.4\( \times \)10\(^{-5}\) mol); \(N_A\) is the avogadro constant (6.022\( \times \)10\(^{23}\)); \(h\) is the Planck constant (6.626\( \times \)10\(^{-34}\) J\( \cdot \)s); \(c\) is the speed of light (3.0\( \times \)10\(^8\) m/s); \(S\) is the irradiation area (6.25 cm\(^2\)); \(P\) is the incident light intensity at certain wavelength (3.4\( \times \)10\(^{-2}\) W\( \cdot \)cm\(^2\)); \(t\) is the irradiation time (1800 s); \(\lambda\) is the monochromatic light wavelength (450 nm).

Therefore, the AQE for the formation of \(N\)-benzylidenebenzylamine over TpTt-COF was calculated to be ca. 13.1%. It outperformed other photocatalysts previously studied under similar experimental conditions, whose AQY was reported to be less than 11%, as shown in Table S1.

**Table S1.** Comparisons of AQE values of different catalysts for benzylamine oxidation under visible light irradiation

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3. ¹H NMR spectra of the obtained condensation products

*N-Benzylidenebenzylamine (1):* The crude product 1 was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5: 1). Depurated product 1 was identified by ¹H NMR spectrum (see Figure S2. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.43 (s, 1 H, Ar-CH=N-), 7.83-7.29 (m, 10 H, ArH), 4.86 (s, 2 H, Ar-CH₂-N-).

![Figure S2. ¹H NMR spectrum of product 1](image-url)
**N-(4-Methylbenzylidene)-p-methylbenzylamine** (2): The crude product 2 was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5: 1). Depurated product 2 was identified by ¹H NMR spectrum (see Figure S3). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.37 (s, 1 H, Ar-CH=NC-), 7.70-7.17 (m, 8 H, ArH), 4.80 (s, 2 H, Ar-CH₂-N=C-), 2.41 (s, 3 H, C₃H₃), 2.36 (s, 3 H, CH₃-Ar-).

![Figure S3. ¹H NMR spectrum of product 2](image)

**N-(4-Methoxybenzylidene)-p-methoxybenzylamine** (3): The crude product 3 was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5: 1). Depurated product 3 was identified by ¹H NMR spectrum (see Figure S4). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.33 (s, 1 H, Ar-CH=NC-), 7.76-6.90 (m, 8 H, ArH), 4.76 (s, 2 H, Ar-CH₂-N=C-), 3.87 (s, 3 H, CH₃-O-Ar), 3.83 (s, 3 H, CH₂-O-Ar).
**Figure S4.** $^1$H NMR spectrum of product 3

$N$-(4-tert-Butylbenzylidene)-$p$-tert-butylbenzylamine (4): The crude product 4 was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5:1). Depurated product 4 was identified by $^1$H NMR spectrum (see Figure S5). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 8.39 (s, 1 H, Ar-CH=N-), 7.76-7.30 (m, 8 H, ArH), 4.81 (s, 2 H, Ar-CH$_2$N=C=), 1.36 (s, 9 H, (CH$_3$)$_2$C-), 1.34 (s, 9 H, (CH$_3$)$_2$C-).

**Figure S5.** $^1$H NMR spectrum of product 4
**N-(4-Fluorobenzylidene)-p-fluorobenzylamine (5):** The crude product 5 was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5: 1). Depurated product 5 was identified by $^1$H NMR spectrum (see Figure S6). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 8.38 (s, 1 H, Ar-CH=N=), 7.81-7.04 (m, 8 H, ArH), 4.79 (s, 2 H, Ar-CH$_2$-N=C=).

![Figure S6. $^1$H NMR spectrum of product 5](image)

**N-(2-Fluorobenzylidene)-o-fluorobenzylamine (6):** The crude product 6 was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5: 1). Depurated product 6 was identified by $^1$H NMR spectrum (see Figure S7). $^1$H NMR (500 MHz, CDCl$_3$) δ (ppm): 8.76 (s, 1 H, Ar-CH=N=), 8.06-7.09 (m, 8 H, ArH), 4.91 (s, 2 H, Ar-CH$_2$-N=C=).
H, -C=\text{N}-), 7.45-7.01 (m, 6 H, -S-C\text{H}-), Depurated product 7 by chromatography on silica gel (petroleum ether/ethyl acetate, 5: 1). Depurated product 7 was identified by \textsuperscript{1}H NMR spectrum (see Figure S8). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 8.45 (s, 1 H, -CH=\text{N}-), 7.45-7.01 (m, 6 H, -S-CH-CH-CH-C-), 4.98 (s, 2 H, -CH\textsubscript{2}-N=C-).

**Figure S7.** \textsuperscript{1}H NMR spectrum of product 6

\textit{-Thiophen-2-yl}\text{-N-(thiophen-2-ylmethyl)methanimine} (7): The crude product 7 was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5: 1). Depurated product 7 was identified by \textsuperscript{1}H NMR spectrum (see Figure S8). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm): 8.45 (s, 1 H, -CH=\text{N}-), 7.45-7.01 (m, 6 H, -S-CH-CH-CH-C-), 4.98 (s, 2 H, -CH\textsubscript{2}-N=C-).

**Figure S8.** \textsuperscript{1}H NMR spectrum of product 7
References


